

STATOIL

Denne rapport
tilhører

STATOIL

L&U DOK. SENTER

L. NR. 20088390066

KODE Well 31/2-2 nr 49

Returneres etter bruk

<p>REPORT TITLE</p> <p>Crude oil - Source Rock Correlation Well 31/2-2.</p>	
<p>CLIENT</p> <p>Norske Shell A/S</p>	
<p>CLIENT'S REF.:</p> <p>Ian Willis</p>	<p>REPORT NO.:</p> <p>O-271/80/2</p>

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CONTINENTAL SHELF INSTITUTE

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Crude oil - Source Rock Correlation Well 31/2-2.	
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Ian Willis	O-271/80/2

AUTHOR (S): M. Bjørøy	DATE: 24.11.80	PROJECT NO.:
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SUMMARY:

Comparison of mass spectra data of saturated and aromatic hydrocarbons from crude oil K 4924 with those from samples K 2875 and K 2876 indicates that 1) the core samples are markedly immature to have been the source rocks for the crude oil, and 2) there is evidence for biodegradation of the crude oil (as indicated by the paucity of n-alkanes of shorter chain length than nC_{17}). Therefore it appears that, if 2875 and/or 2876 were the source of 4924 then extensive alternation of the oil has taken place.

KEY WORDS

Oil - Source Rock

Correlation

SOURCE-ROCK CRUDE OIL CORRELATION, WELL 31/2-2.

EXPERIMENTAL

Extraction:

Of the core samples, approximately 100 gm of each was extracted in a flow through system (Radke et al., 1978 (Anal. chem. 49, 663-665) for 10 min. using dichloromethane (DCM) as solvent. The DCM used as solvent was distilled in an all glass apparatus to remove contaminants.

Activated copper fillings were used to remove any free sulphur from the samples.

After extraction, the solvent was removed on a Buchi Rotavapor and transferred to a 50 ml flask. The rest of the solvent was then removed and the amount of extractable organic matter (EOM) determined.

Chromatographic Separation

The extractable organic matter (EOM) was separated into saturated fraction, aromatic fraction and non hydrocarbon fraction using a MPLC system with hexane as eluant (Radke et al., Anal. chem., 1980). The various fractions were evaluated on a Buchi Rotavapor and transferred to glass-vials and dried in a stream of nitrogen. The crude oil was separated using the same system.

Gas chromatographic analyses

The saturated and aromatic HC fractions were diluted with n-hexane and analysed on a HP 5730 A gas chromatograph, fitted with a 25 m OV101 glass-capillary column and an automatic injection system. Hydrogen (0.7 ml/min.) was used as carrier gas and the injection was performed in the split mode (1:20), and temperature programmed 60-260° at 4°/min. The crude oil was analysed on the same GC system but temperature programmed 0-260° at 4°/min.

GC/MS Analysis

Sixteen saturated hydrocarbon fractions were analysed by Selected Ion

Monitoring (SIM) and Sequential Scanning using a VG-Micromass 70-70 double focusing magnetic mass spectrometer coupled directly to a Pye 204 gas chromatograph via an all glass line. A 20 metre by 0.3 mm I.D. glass capillary column coated with OV-1 was temperature programmed from 120°C to 260°C at 4°C/min. with helium carrier gas at a flow rate of 1 ml/minute. Data acquisition was by a VG-data Systems "Multispec" data system. The sequential scanning was performed at 1 sec/decade and SIM recording at 200 m/sec dwell time per ion.

RESULTS AND DISCUSSION

GC-analyses

The oil was analysed gas chromatographically and is found to have a strange pattern, especially in the low to medium hydrocarbon range, where hardly any n-alkanes are detected. This is believed to be due to bacteriological activity. The same pattern is seen when the saturated hydrocarbon fraction (C₁₅+) is analysed. The aromatic hydrocarbon fraction shows well separated hydrocarbons in the medium molecular weight area while the high molecular weight area is very complex and hardly any separation is seen.

The gas chromatograms of both the saturated and aromatic hydrocarbons of the two core samples vary considerably from those of the whole oil. This is due to the core samples being immature.

GC-MS Analyses

Saturated Fraction

The saturated hydrocarbon fraction of the oil sample K 4924 was examined by full data collection for a) comparison of triterpane and sterane distribution with those obtained for the extracts from the two core samples and b) the determination of the presence or absence of the C₂₈ triterpane (m⁺ 384) found in several other oils from the North Sea. Thus mass chromatograms for m/z 217, 191, 370, 384, 398 and 412 were obtained. The saturated fractions of the extracts from the cores were run in MID mode and mass chromatograms for m/z 217 and 191 were obtained.

M/z 217 (Steroidal alkanes)

The major components in the two extracts are the regular steranes (pk. 5 cholestane, pk. 7 24-methylcholestane and pk. 9, 24-ethylcholestane). This would indicate a relatively low maturity. Both the visual distribution of steroidal alkanes and indeed the calculated relative distribution (relative to the 24-Ethylcholestane) show that sample K 4924 contains a major contribution of rearranged steranes compared to regular steranes. Such an observation is in direct contrast with the distribution observed for samples K 2875 and K 2876.

m/z 191 (Triterpenoid alkanes)

The triterpane distribution (m/z 191) for the two extracts, K 2875 and K 2876 are very similar to each other, and show a typical distribution for immature samples in the $C_{31} - C_{35}$ region. Marked on the m/z 191 chromatogram are the carbon skeleton assignments of the major triterpanes present in K 4924, based on molecular ion mass fragmentography (i.e. m/z 370, 384, 398 and 412). Of particular interest is the presence of minor amounts of the C_{28} triterpane presumably 28, 30 - bisnorhopane. The spectrum of this component, although clearly a mixture, shows the ions at m/z 163 and 177 together with the molecular ion (m/z 384) characteristic of 28, 30 - bisnorhopane.

The relative distribution of triterpanes in this sample is dissimilar to those observed previously for K 2875 and K 2876. Indeed, the distribution observed is typical for most crudes unlike those for K 2875 and K 2876.

Aromatic Fractions

The aromatic fraction from the two extracts and the oil were examined by full data collection, and the relative distribution of certain polynuclear aromatics determined. Thus, the T.I.C. and massfragmentograms for m/z 141, 178, 184, 192 and 206 were obtained, and the results from the three samples compared.

F.D.C. of samples K 4924 AROMATICS

m/z 141 (alkylnaphthalenes)

The m/z 141 chromatogram shows that the major components present in the T.I.C of the fraction are monoalkyl and dialkylnaphthalenes. These components were not present in the samples examined for 2875 and 2876.

m/z 178 (phenanthrene)

The m/z 178 chromatogram shows the presence of a major component attributed to phenanthrene, similar to the traces obtained for 2875 and 2876.

m/z 184 (dibenzothiophene)

A single major peak in the m/z 184 chromatogram at the retention time of dibenzothiophene was not observed in K 4924, such a component was present in both 2875 and 2876.

m/z 192 (methylphenanthrene)

The m/z 192 chromatogram shows the presence of the 2 major methylphenanthrene isomers shown also to be present in samples 2875 and 2876. However, the relative distribution of the isomers in K 4924 does not compare with those 2875 and 2876.

m/z 206 (dimethylphenanthrenes)

The m/z 206 chromatogram shows an isomer distribution similar to those obtained for 2875 and 2876. The major differences observed in the distribution of alkylnaphthalenes, dibenzothiophene and methylphenanthrene isomers suggests a source for K 4924 other than 2875 and 2876.

F.D.C. Examination of Samples K 2875 (2nd Sample) AROMATICS

Data are provided for T.I.C. and mass chromatograms m/z 178, 206, 253, 239 and 365. From the T.I.C. it is apparent that a complex mixture of high molecular weight components are present in the sample. The chromatograms

for m/z 178 and 206 were included to demonstrate the reproducibility of the F.D.C. data with those previously obtained by M.I.D. The chromatogram for m/z 253 shows that the components of high abundance at the high molecular weight end of the T.I.C. are without doubt aromatic steranes having 2 methyl groups in the nucleus. Indeed, spectra are included of the major components confirming the above. Further spectra of several of the minor components present in this region show a base peak at m/z 267 suggesting aromatic steranes containing 3 methyl groups. It would therefore appear that for this sample the aromatic steranes were not eluted with the aliphatic hydrocarbons, as is normal for most fractions.

F.D.C. Analysis of sample K 2876 AROMATICS

Data are presented for the T.I.C. and mass chromatograms for m/z 178, 206, 202, 184, 253 and 252. The gas chromatograms for m/z 178 and 206 were included to demonstrate, as for 2875 above, the reproducibility between F.D.C. and M.I.D. The m/z 253 chromatogram shows that very little aromatic sterane components were present in the fraction. The T.I.C. shows at least 2 components of major abundance in the high molecular weight region, one of which (Scan 545) shows an abundant contribution from m/z 252 (See m/z 252 chromatogram). The full mass spectrum of this component is enclosed and is undoubtedly characteristic of a poly nuclear aromatic such as benzfluoranthene, benzpyrene or perylene. Unfortunately it is not possible to distinguish which of the 3 possible structural types to this component belongs on the basis of m.s. alone. If necessary, this could be performed by co-chromatography with authentic standards. The mass spectrum of the components eluting at Scan 576 (enclosed) shows it to be a phthalate ester. The mass spectra of components eluting as a doublet eluting between scans 525 and 535 indicate that these components are aromatic and possibly polynuclear.

Conclusion:

Both the aromatic and aliphatic hydrocarbon data available suggest that K 4924 is a mature oil whereas 2875 and 2876 are relatively immature. Thus, if 2875 and/or 2876 were the source of K 4924 then extensive alteration of the oil has taken place.

T A B L E : I

WEIGHT OF EDM AND CHROMATOGRAPHIC FRACTIONS

I	:	:	Rock	:	:	:	:	Non	:	I
I	IKU-No	DEPTH	Extr.	EDM	Sat.	Ar.o.	HC	HC	TOC	I
I	:	:	:	:	:	:	:	:	:	I
I	:	(m)	(g)	(mg)	(mg)	(mg)	(mg)	(mg)	(%)	I
I	:	:	:	:	:	:	:	:	:	I
I	:	:	:	:	:	:	:	:	:	I
I	K-2875	0	41.3	13.3	2.0	.8	2.8	10.5	2.6	I
I	:	:	:	:	:	:	:	:	:	I
I	K-2876	0	50.0	17.4	2.4	.5	2.9	14.5	2.6	I

T A B L E : II

CONCENTRATION OF EOM AND CHROMATOGRAPHIC FRACTIONS

(Weight ppm of rock)

IKU-No	DEPTH (m)	EOM	Sat.	Aro.	HC	Non HC
K-2875	0	322	48	19	68	254
K-2876	0	348	48	10	58	290

T A B L E : III

CONCENTRATION OF EOM AND CHROMATOGRAPHIC FRACTIONS

(ms/g TOC)

I	:	:	:	:	:	:	:	:	I
I	IKU-No	: DEPTH	: EOM	: Sat.	: Aro.	: HC	: Non	: HC	I
I	:	:	:	:	:	:	:	:	I
I	:	(m)	:	:	:	:	:	:	I
I	:	:	:	:	:	:	:	:	I
I	K-2875	: 0	: 12.3	: 1.9	: .7	: 2.6	: 9.7	:	I
I	:	:	:	:	:	:	:	:	I
I	K-2876	: 0	: 13.3	: 1.8	: .4	: 2.2	: 11.1	:	I

T A B L E : I V

COMPOSITION IN % OF THE MATERIAL EXTRACTED FROM THE ROCK

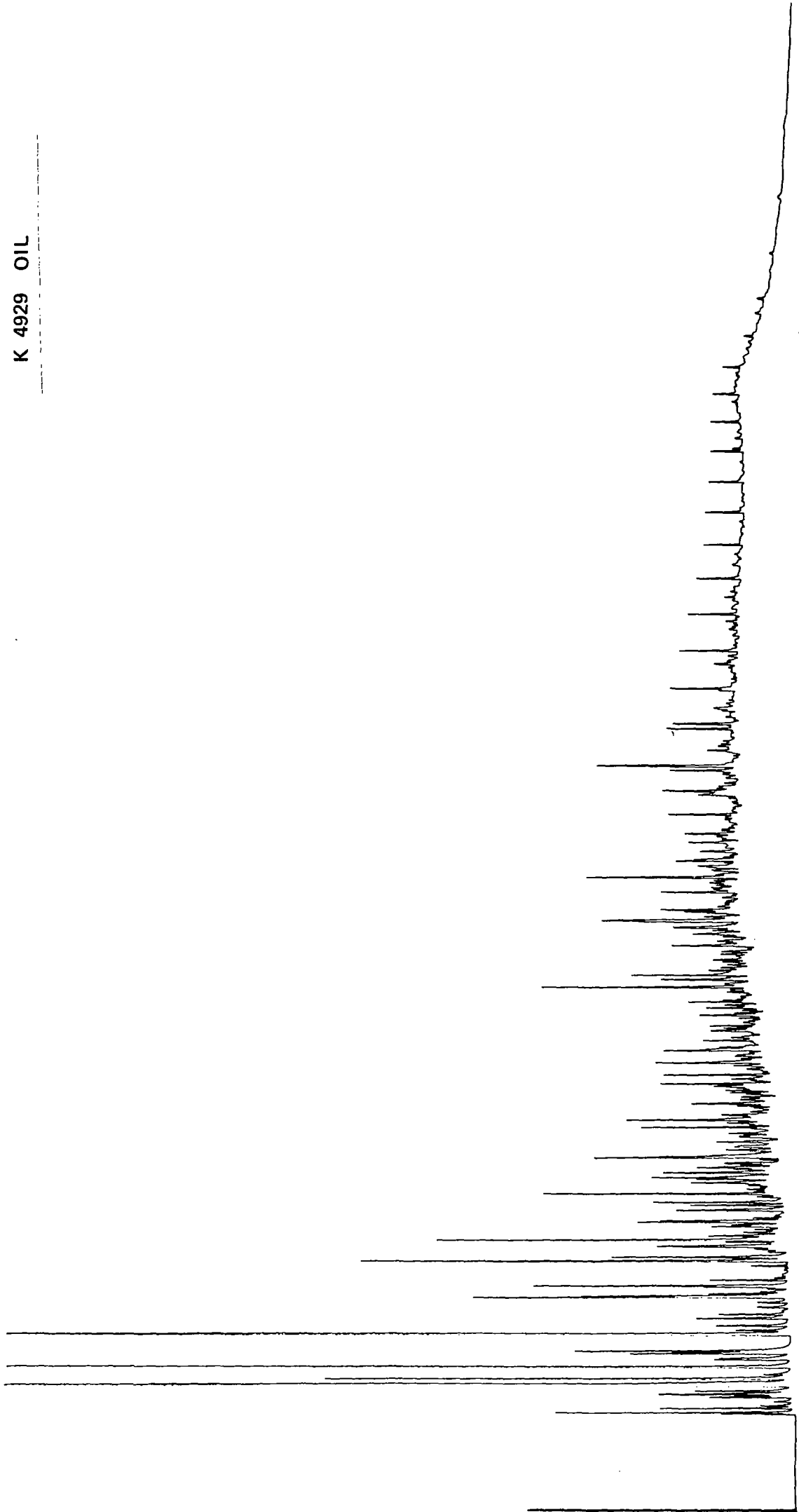
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I	IKU-No	:	DEPTH	:	---	:	---	:	---	:	---	:	---	I
I	:	:	EOM	:	EOM	:	EOM	:	Aro	:	EOM	:	Non HC	I
I	:	(m)	:	:	:	:	:	:	:	:	:	:	:	I
I	K-2875	:	0	:	15.0	:	6.0	:	21.1	:	250.0	:	78.9	I
I	K-2876	:	0	:	13.8	:	2.9	:	16.7	:	480.0	:	83.3	I

Table V

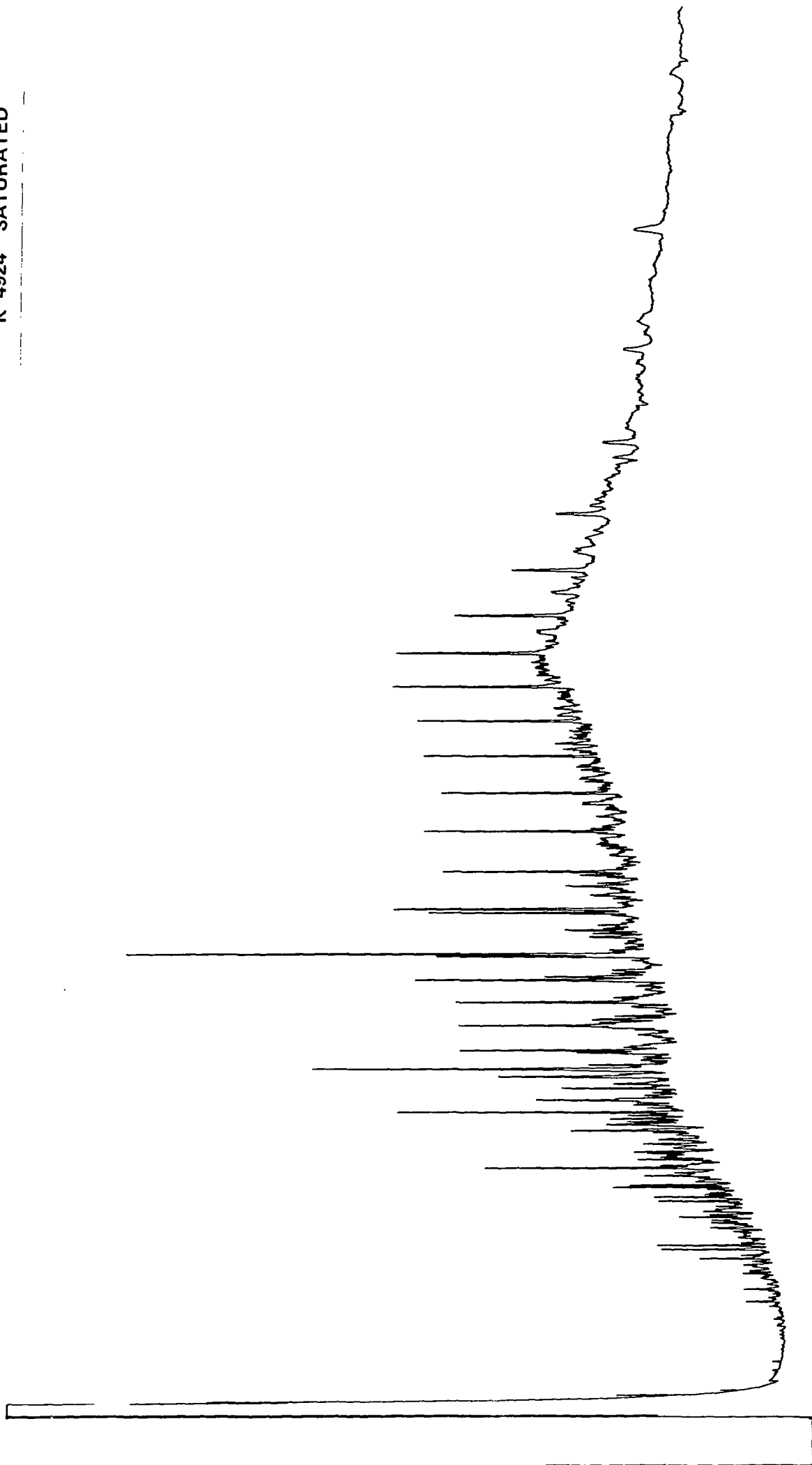
Ratio peaks in sterane profile relative to 24-Ethylcholestane (pk. 9).

Sample	Depth(m)	1	2	3	4	5	6	7	8	9	10	11
K 2875	1516	0.37	0.24	0.47	0.12	1.2	0.43	0.81	0.47	1.0	0.08	0.33
K 2876	1537	0.23	0.18	0.48	0.12	1.25	0.38	0.77	0.45	1.0	0.09	0.43
K 4924	(Oil)	2.8	2.4	1.7	3	0.8	0.6	0.6	1.9	1.0	0.7	0.3

K 4929 OIL



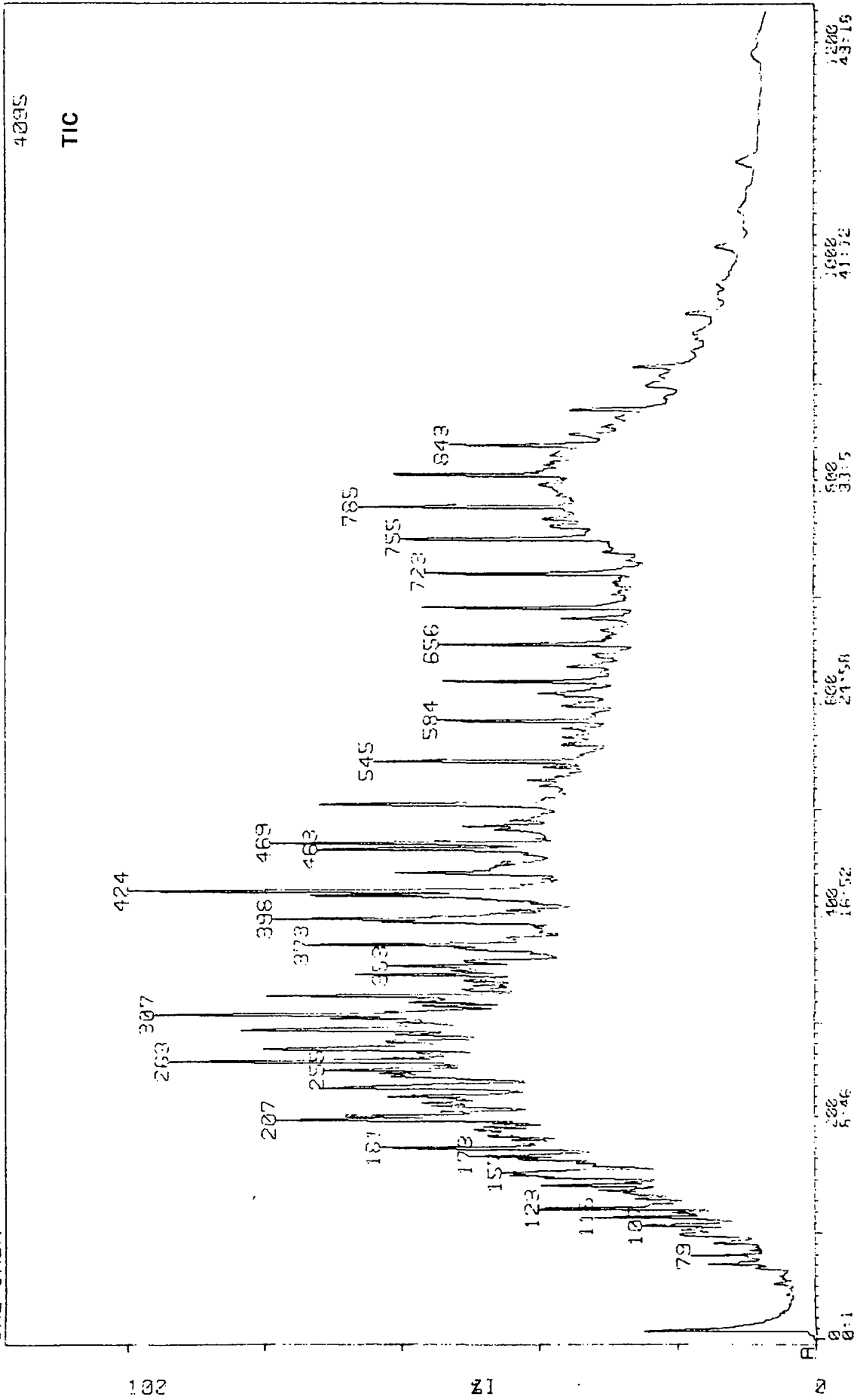
K 4924 SATURATED



K4924 0 - 1250 SAMPLE K4924 SATURATED SAMP

28-AUG-80

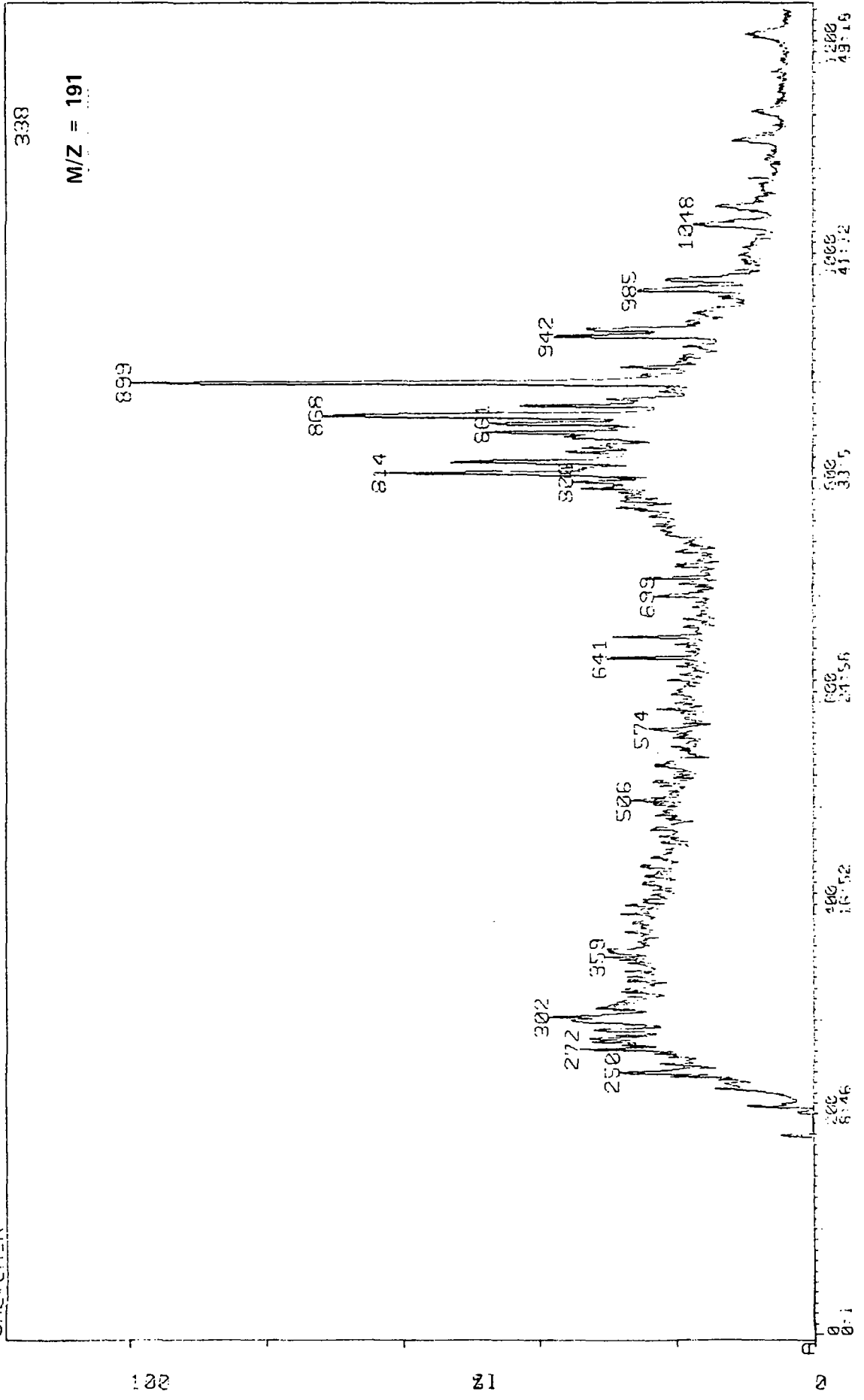
A: ATJC
CAL: CALK



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28-AUG-80

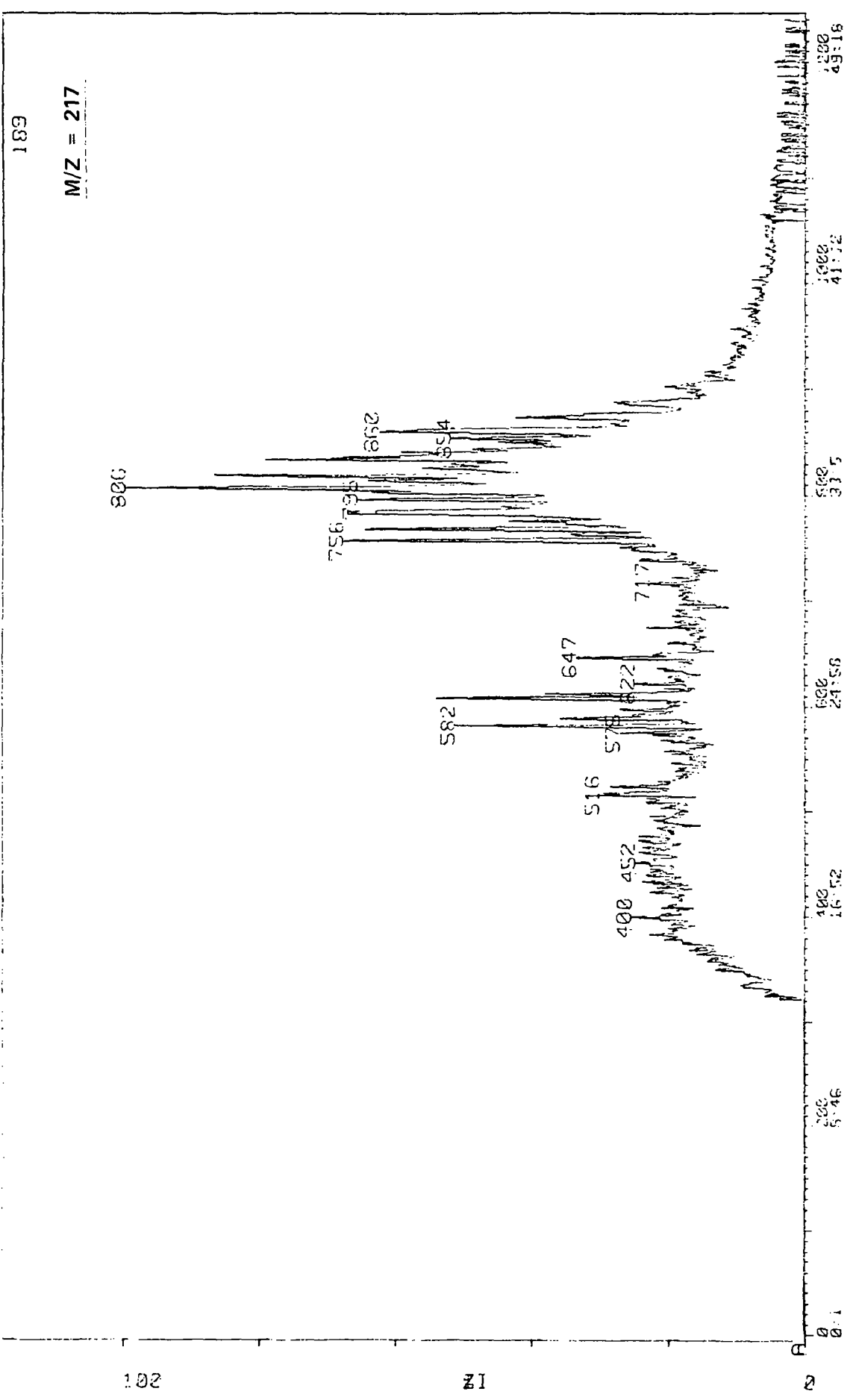
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CAL: CR-K



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28-AUG-80

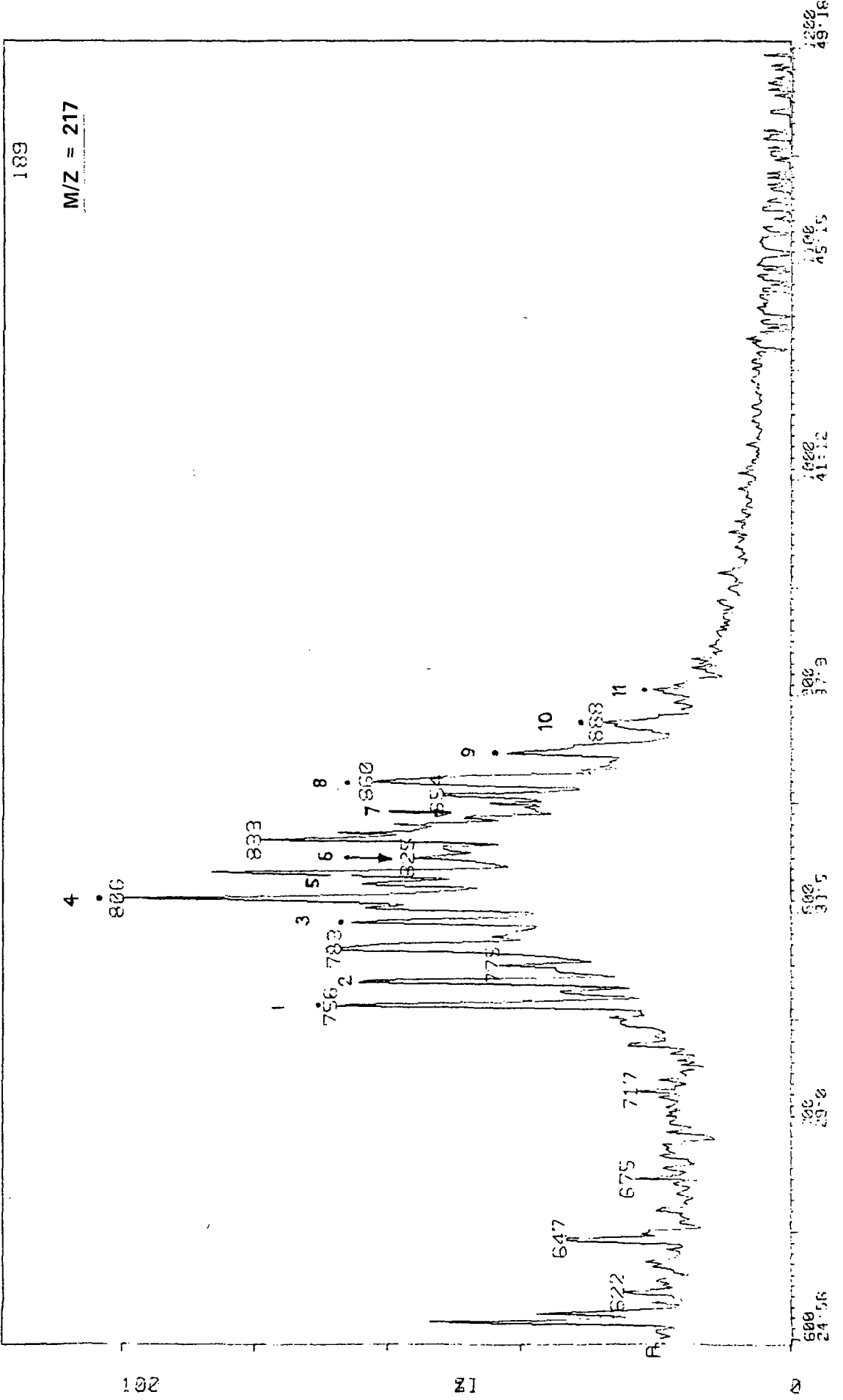
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28-AUG-80

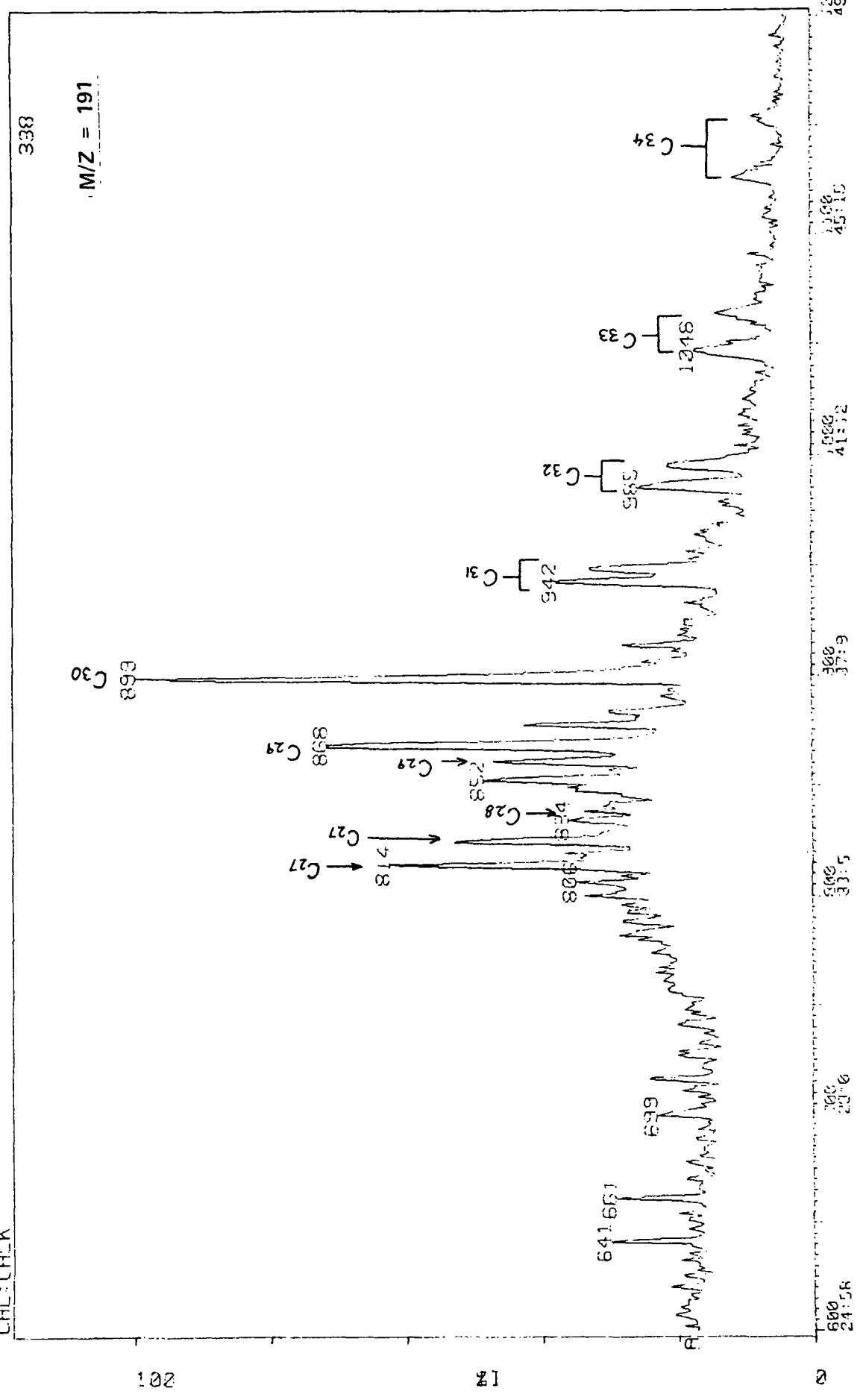
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28-AUG-80

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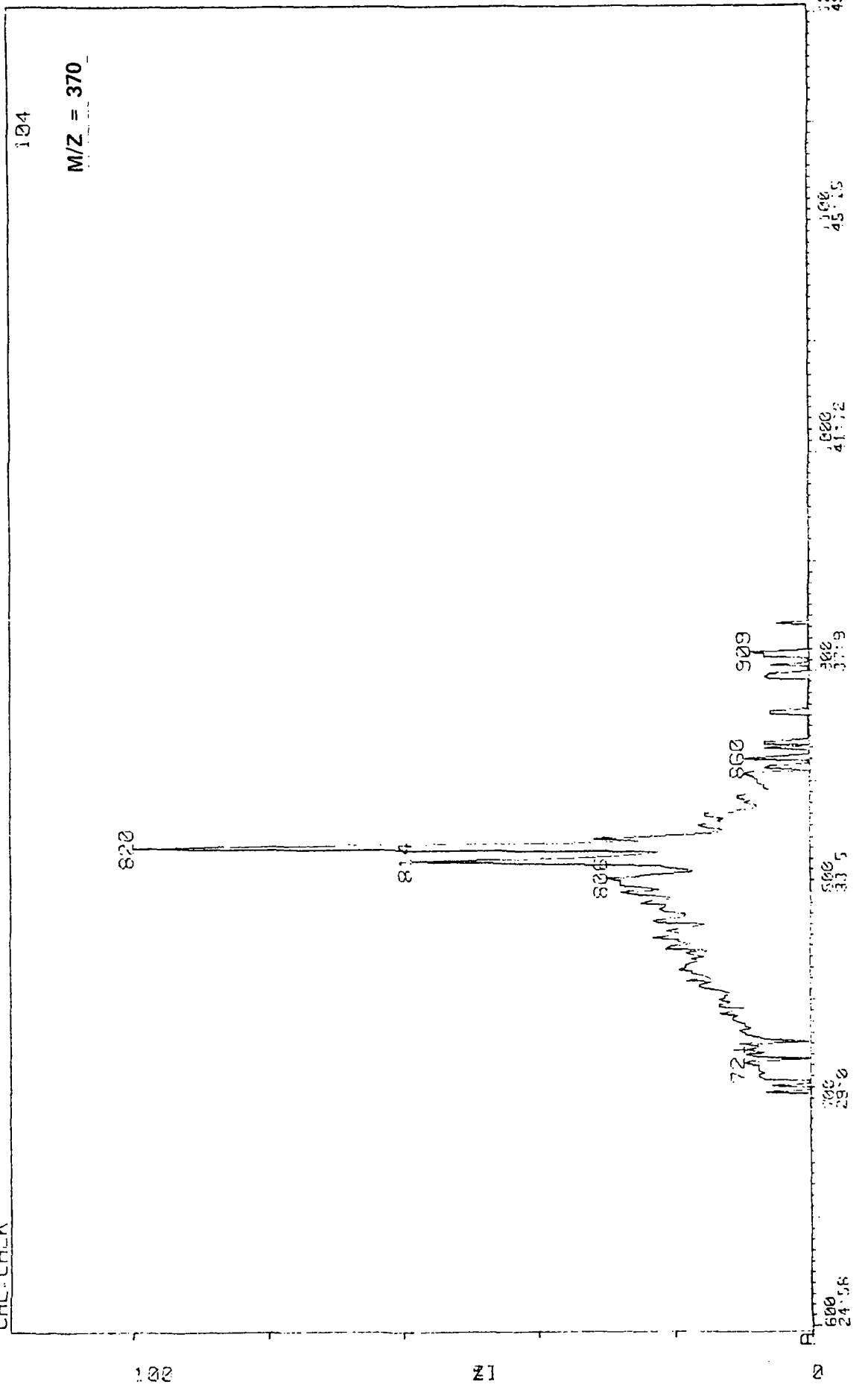
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28-AUG-80

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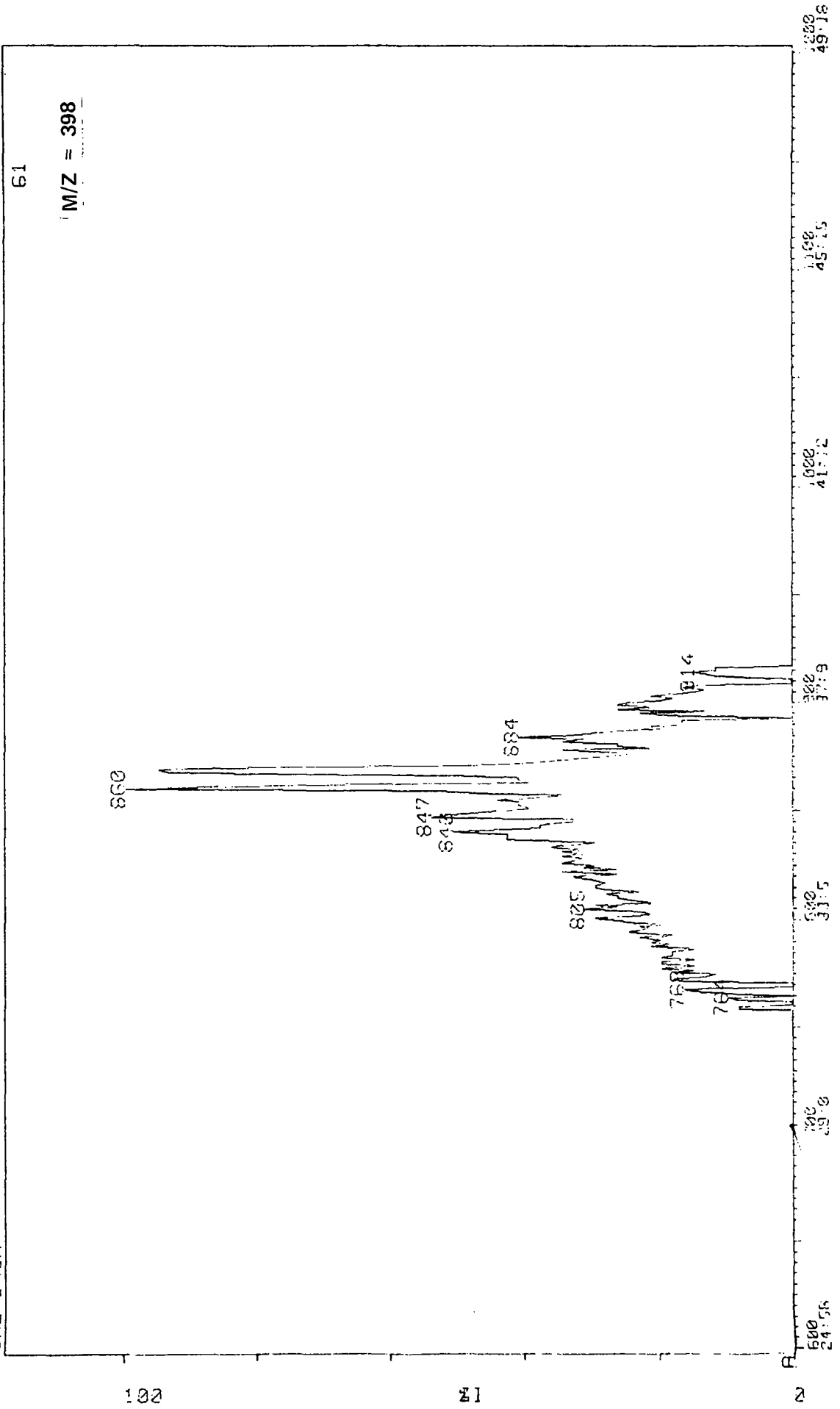
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28-AUG-80

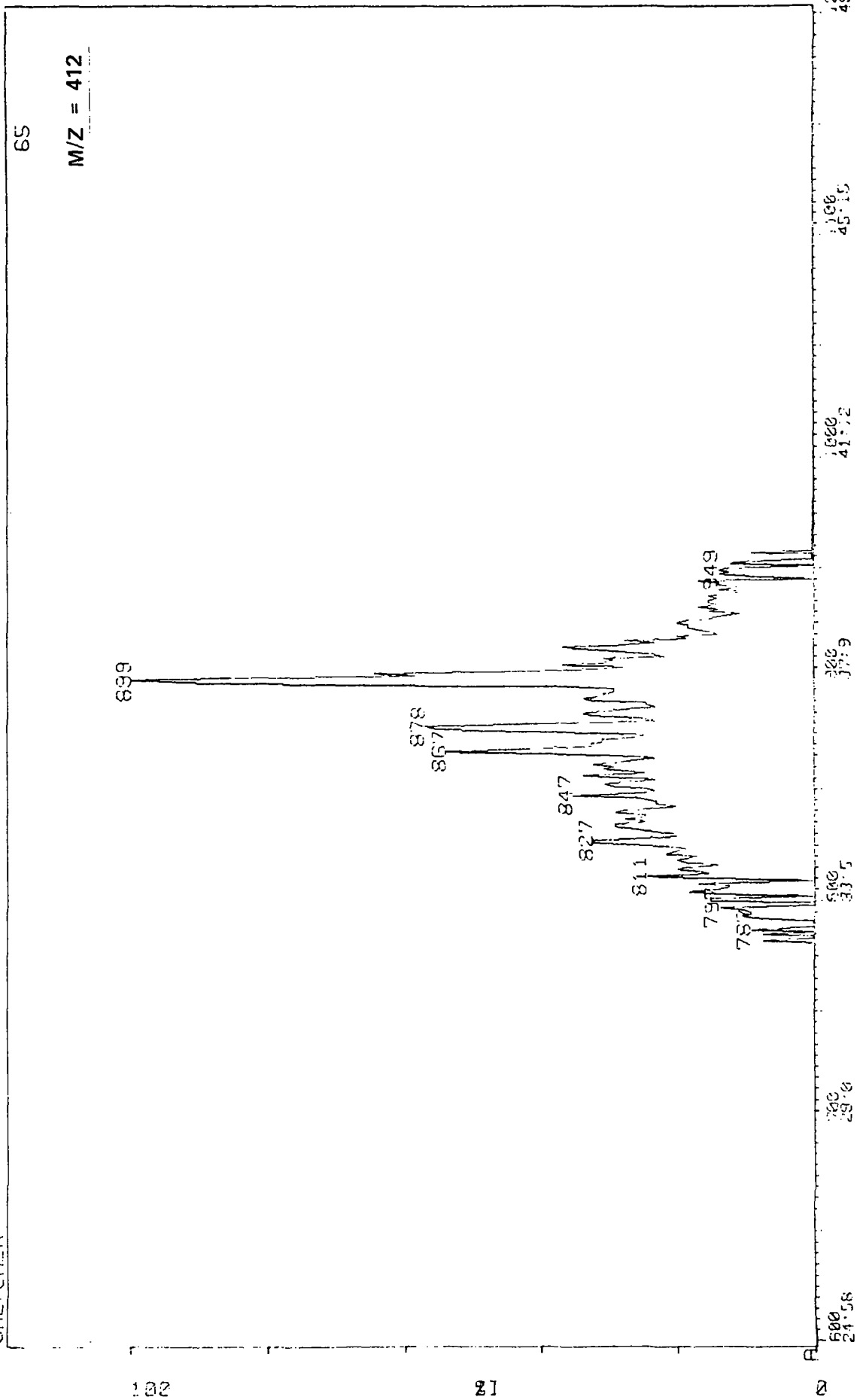
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28-AUG-80

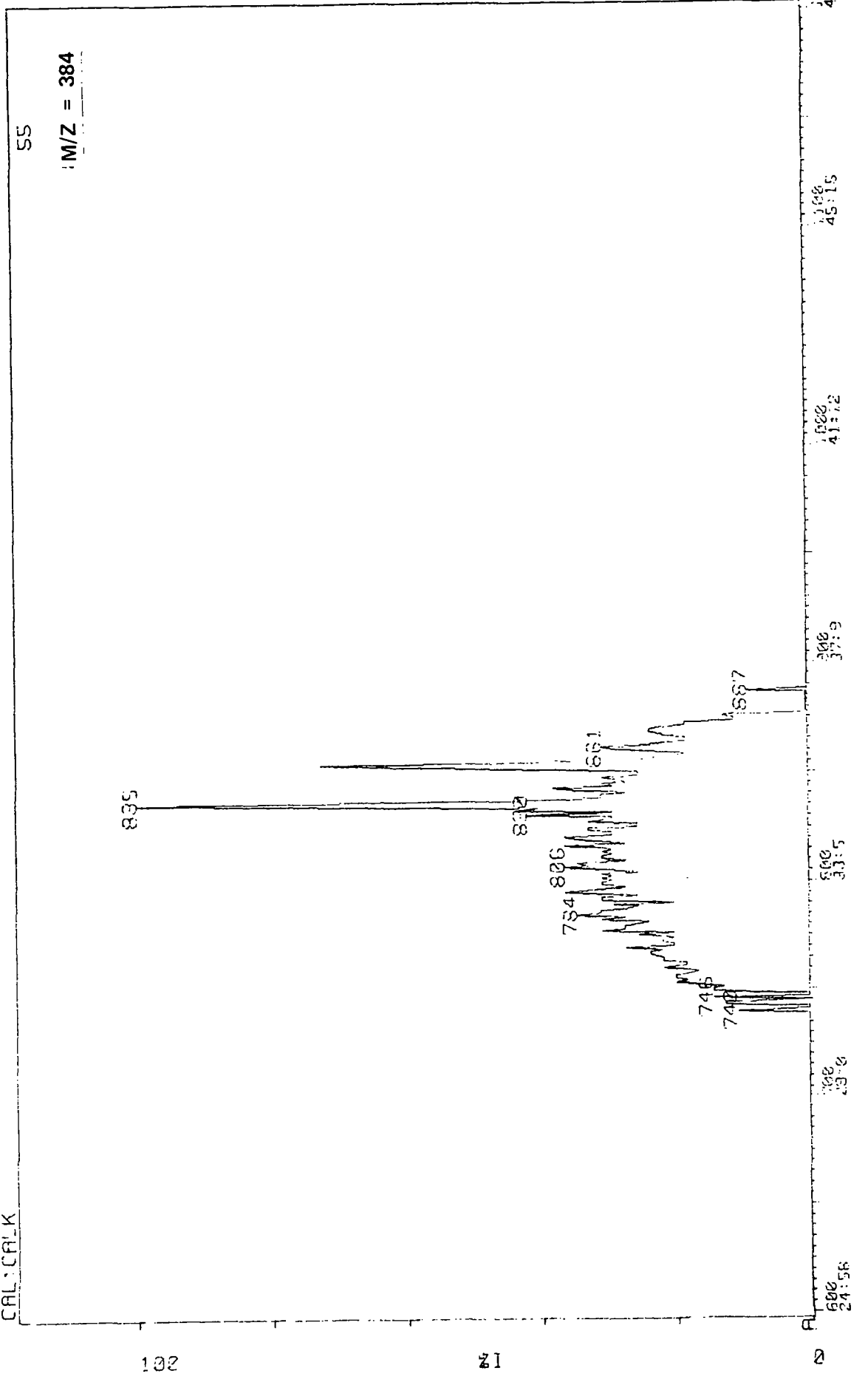
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28-AUG-80

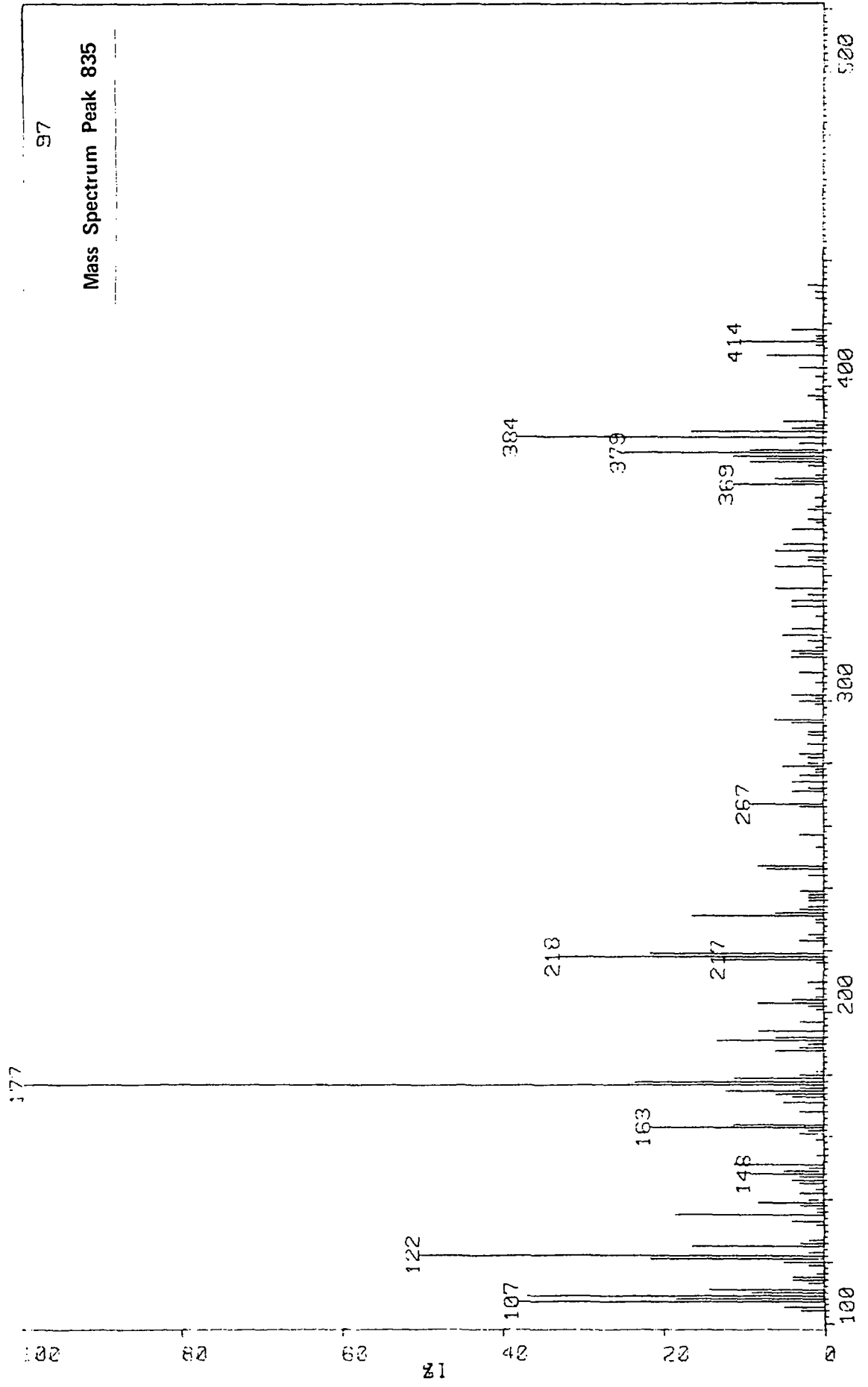
K4924 600--1200 SAMPLE K4924 SATURATED SAMP

R: 384K
CAL: CALK



K4924 835 829.3.6.6.9.11 SAMPLE K4924 SATURATED SAMP
CAL:CALK

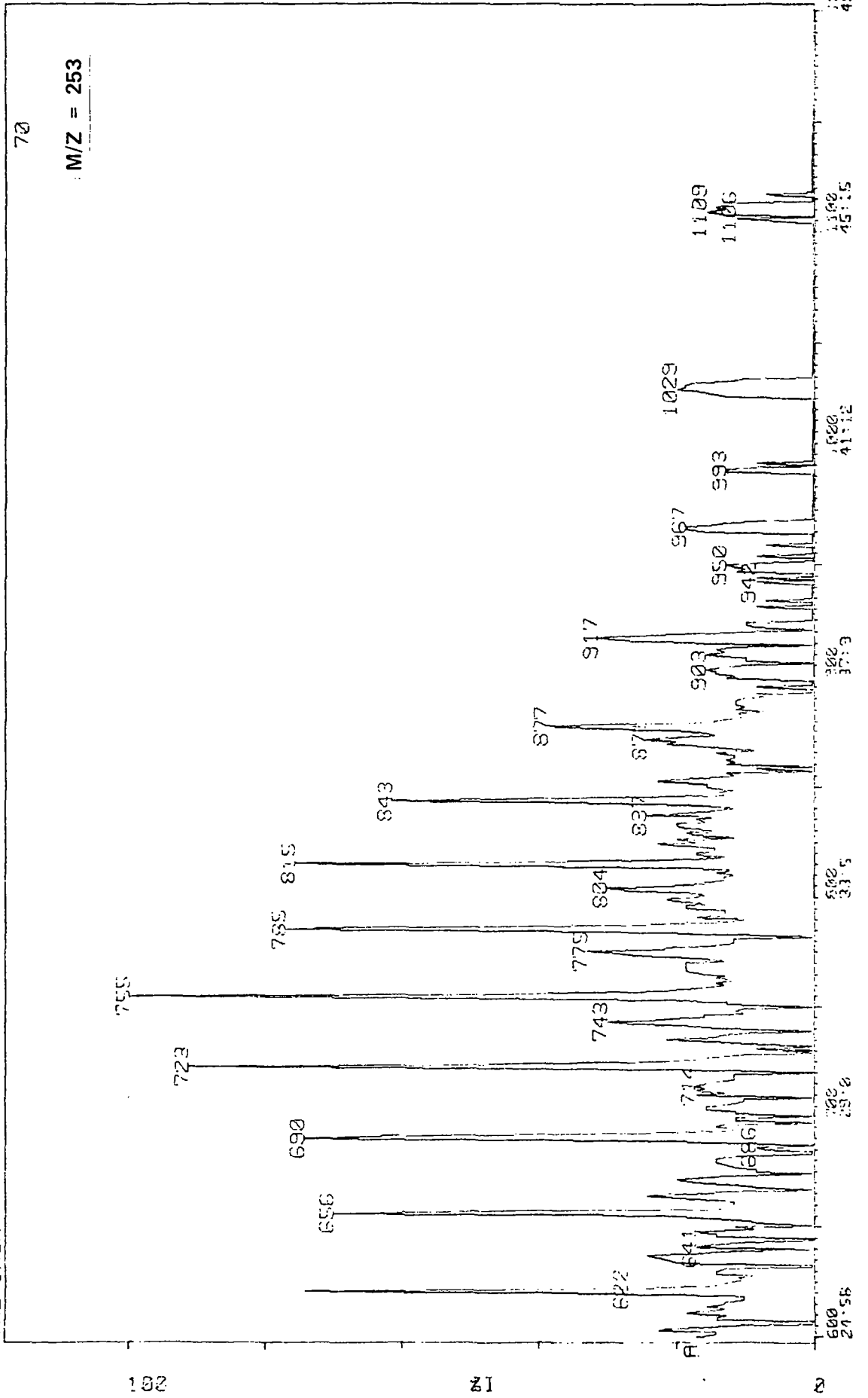
28-AUG-80



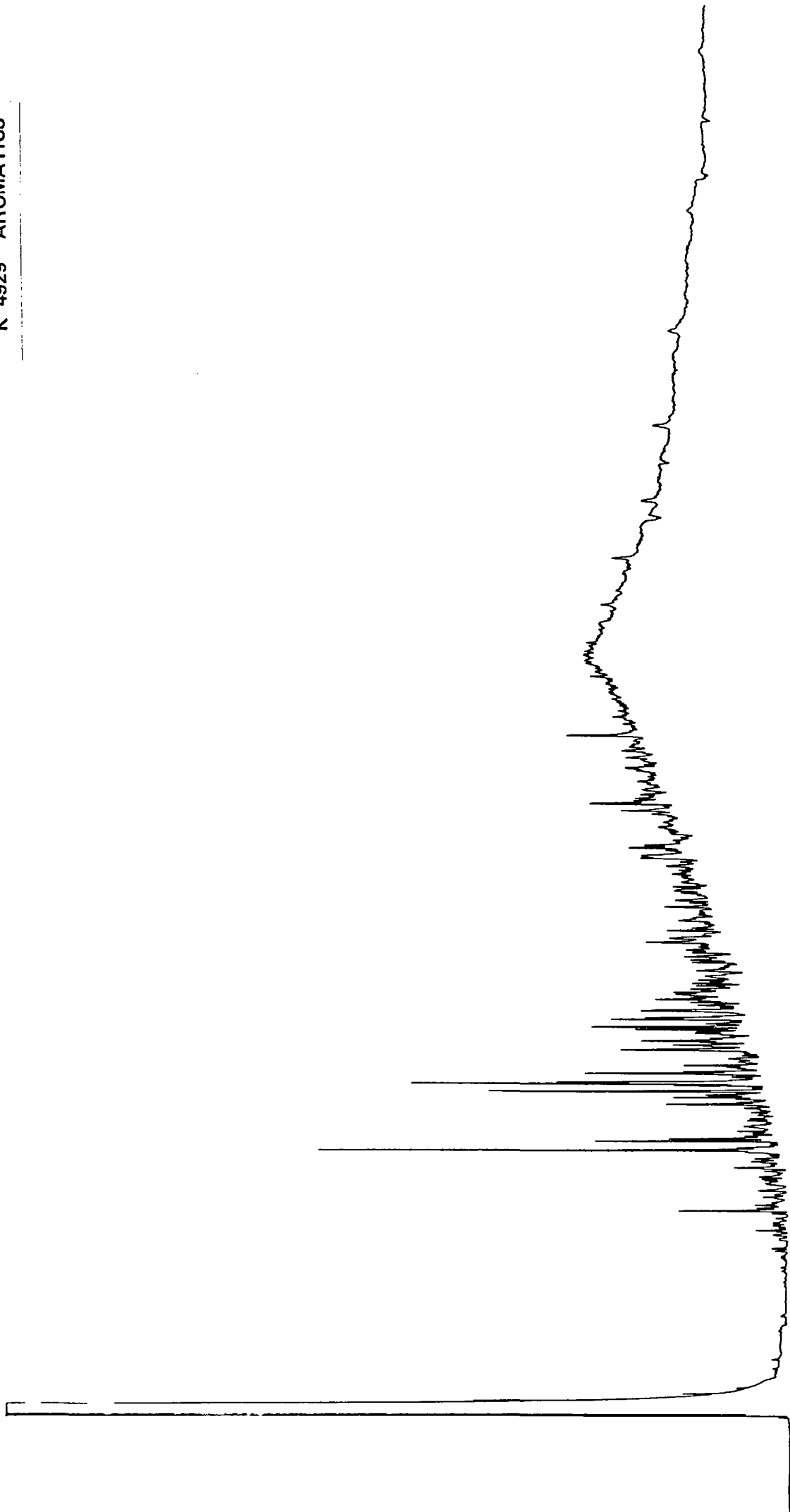
K4924 600 - 1200 SAMPLE K4924 SATURATED SAMP

28-AUG-80

R: 253K1
CAL: CALK



K 4929 AROMATICS

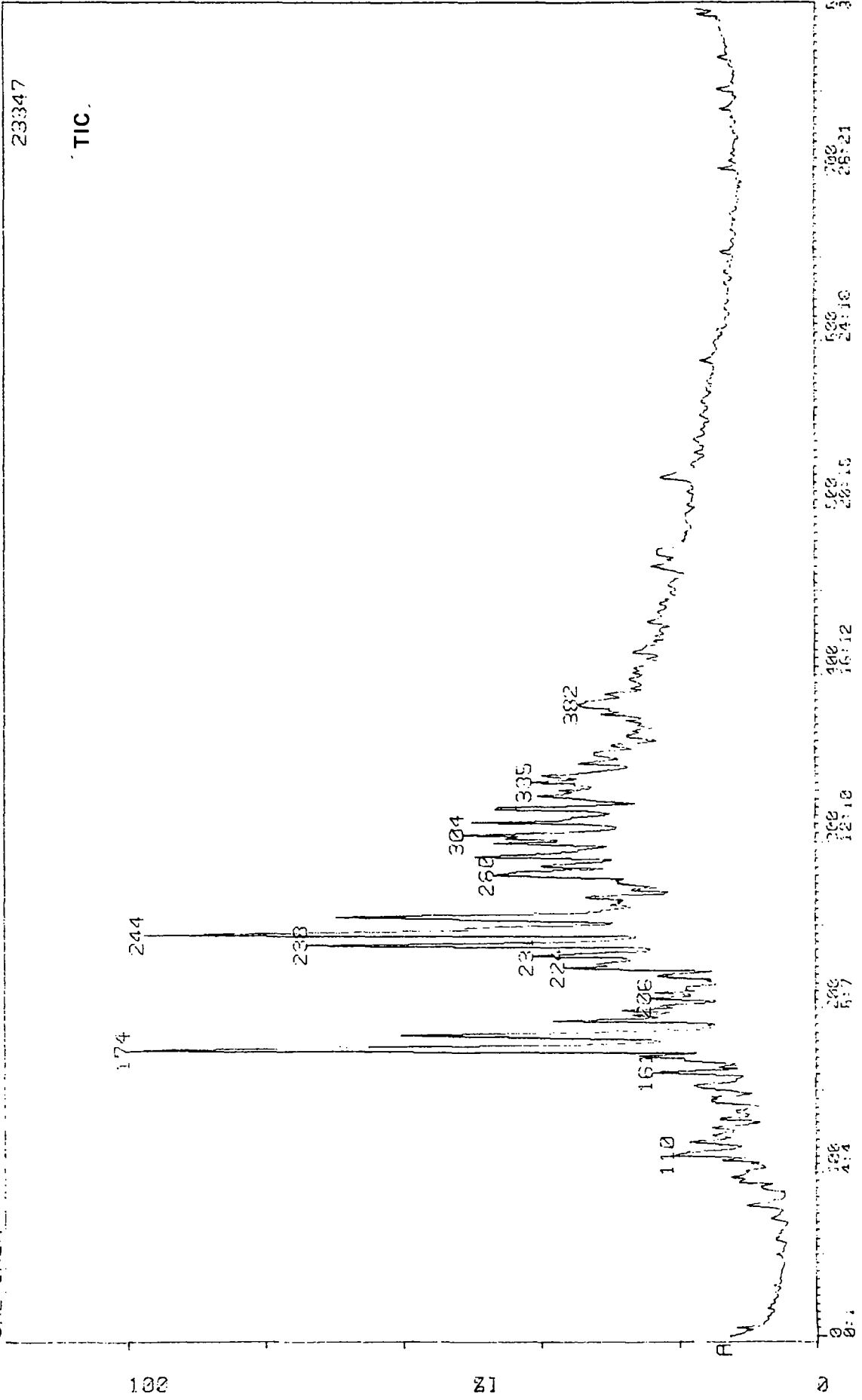


K4924A 0-800 K4924 AROMATIC FRACTION

28-AUG-80

A:TIC

CAL:CALK



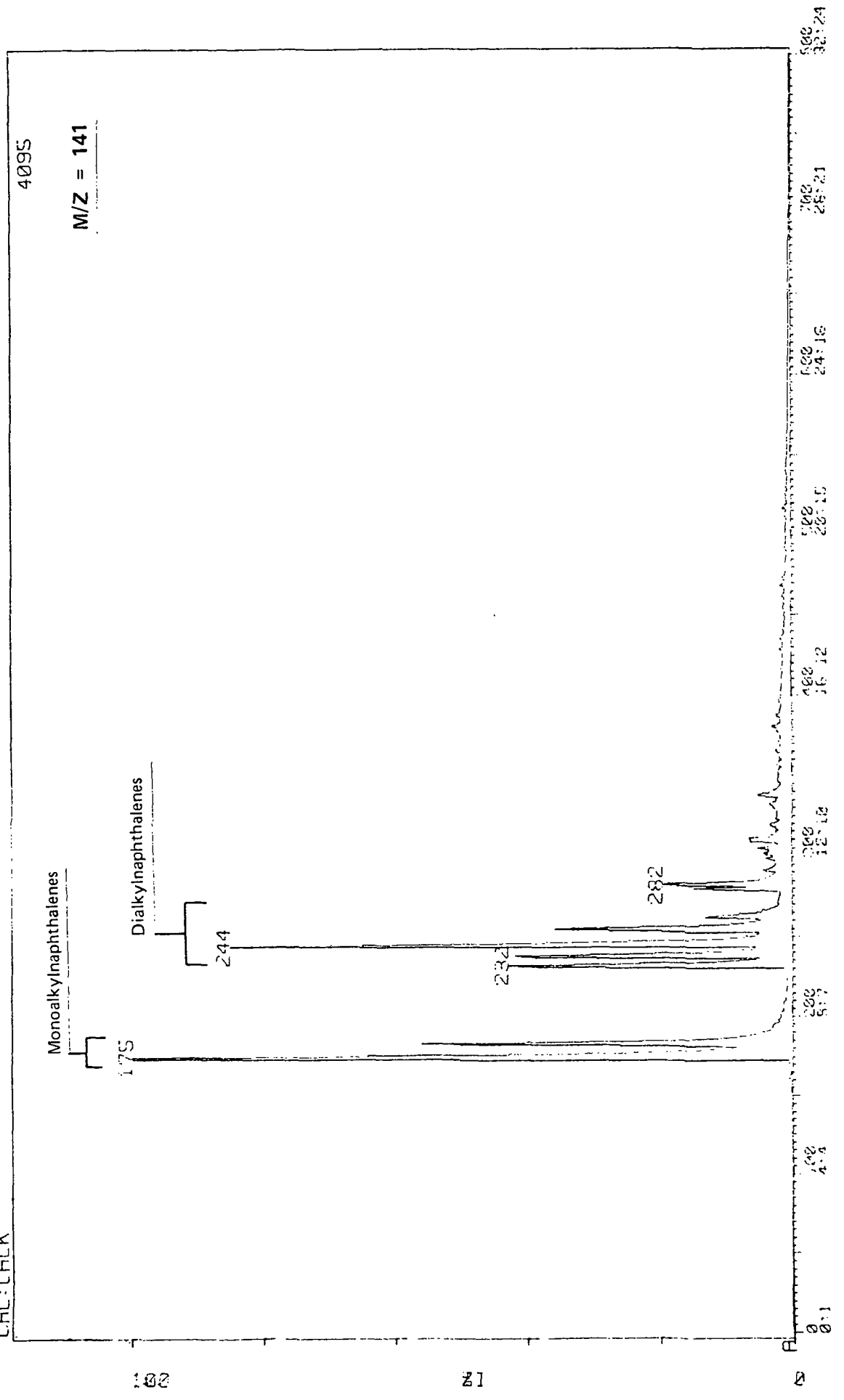
23347

TIC

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28-AUG-80

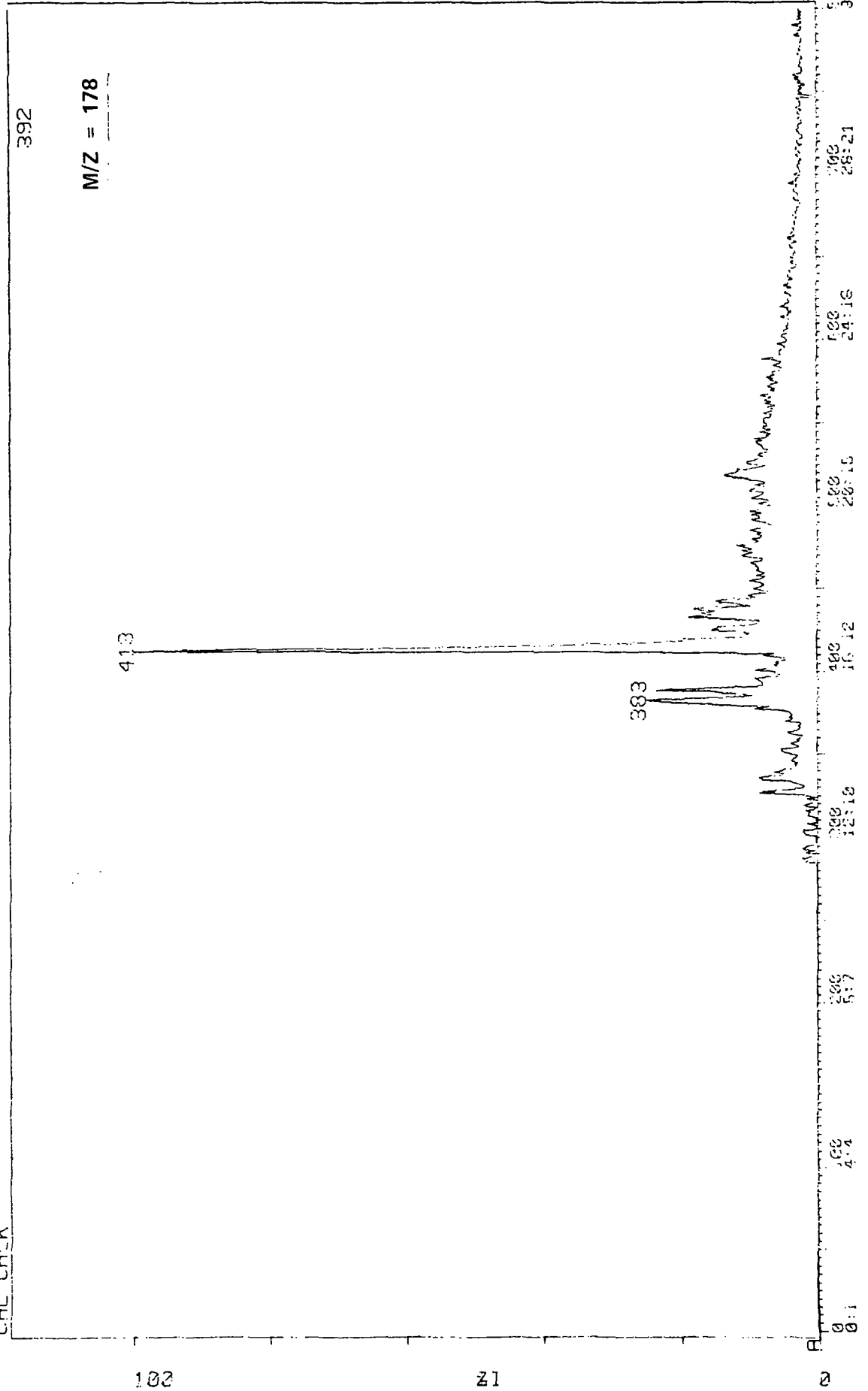
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28-AUG-80

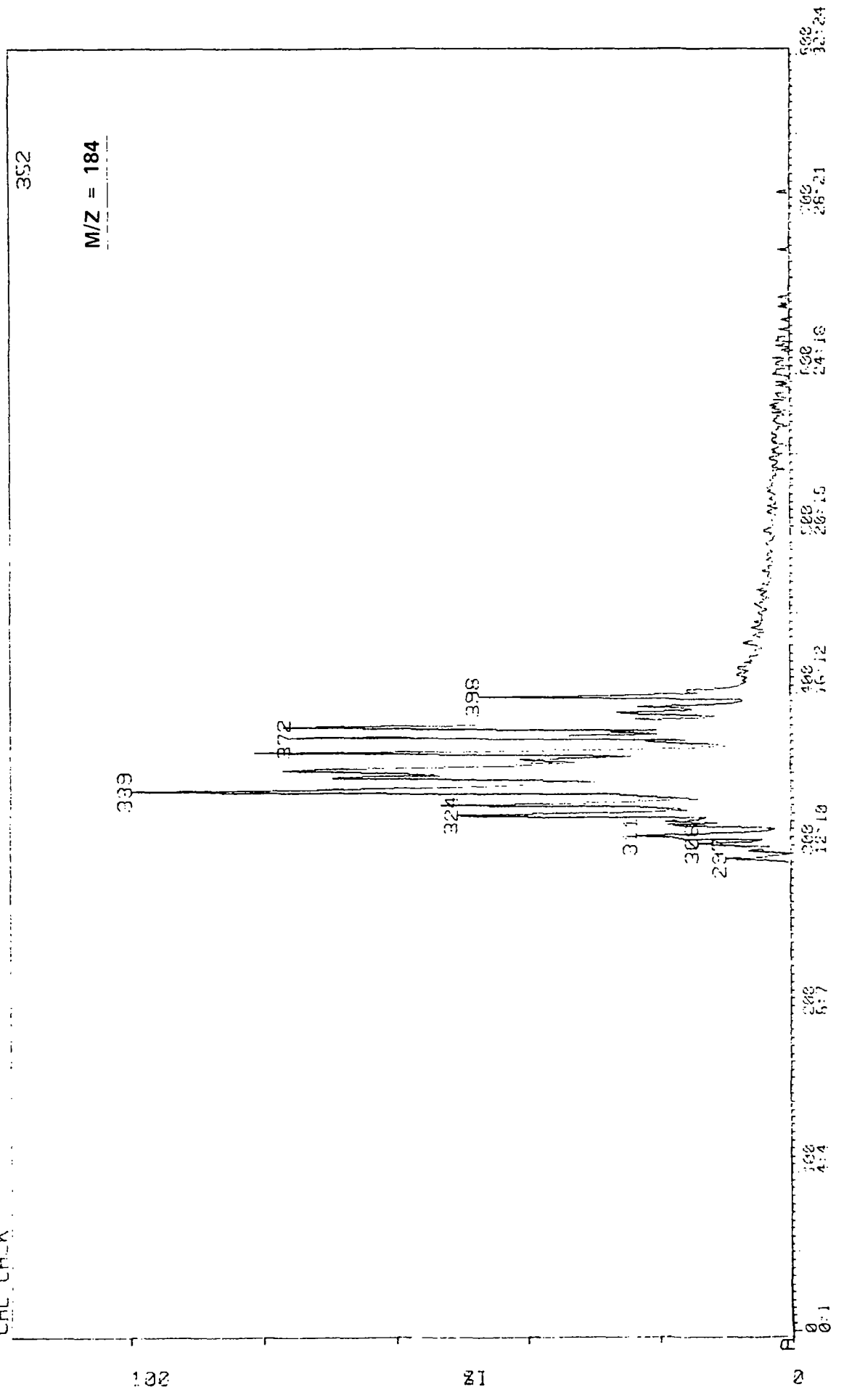
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28-AUG-80

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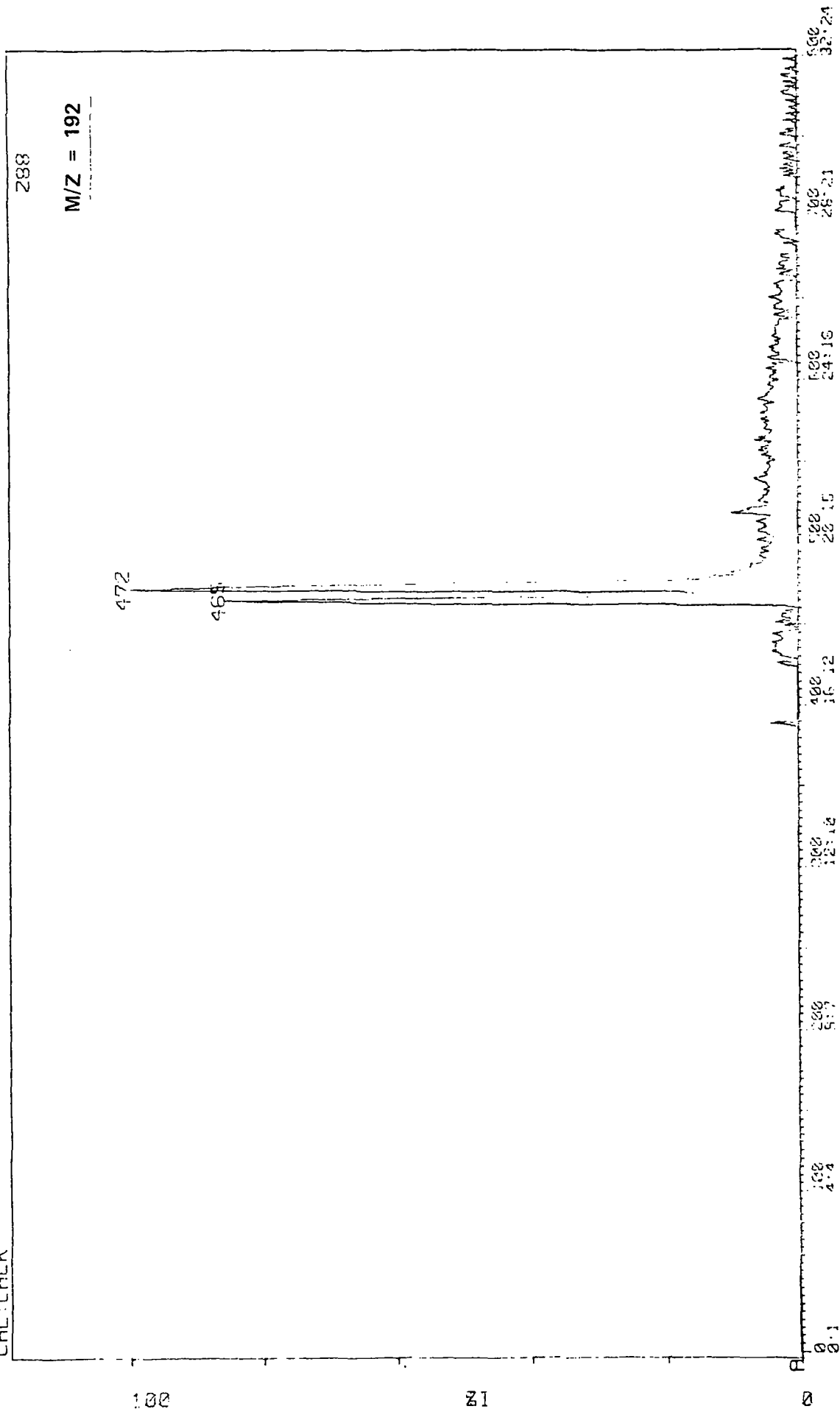


28-AUG-80

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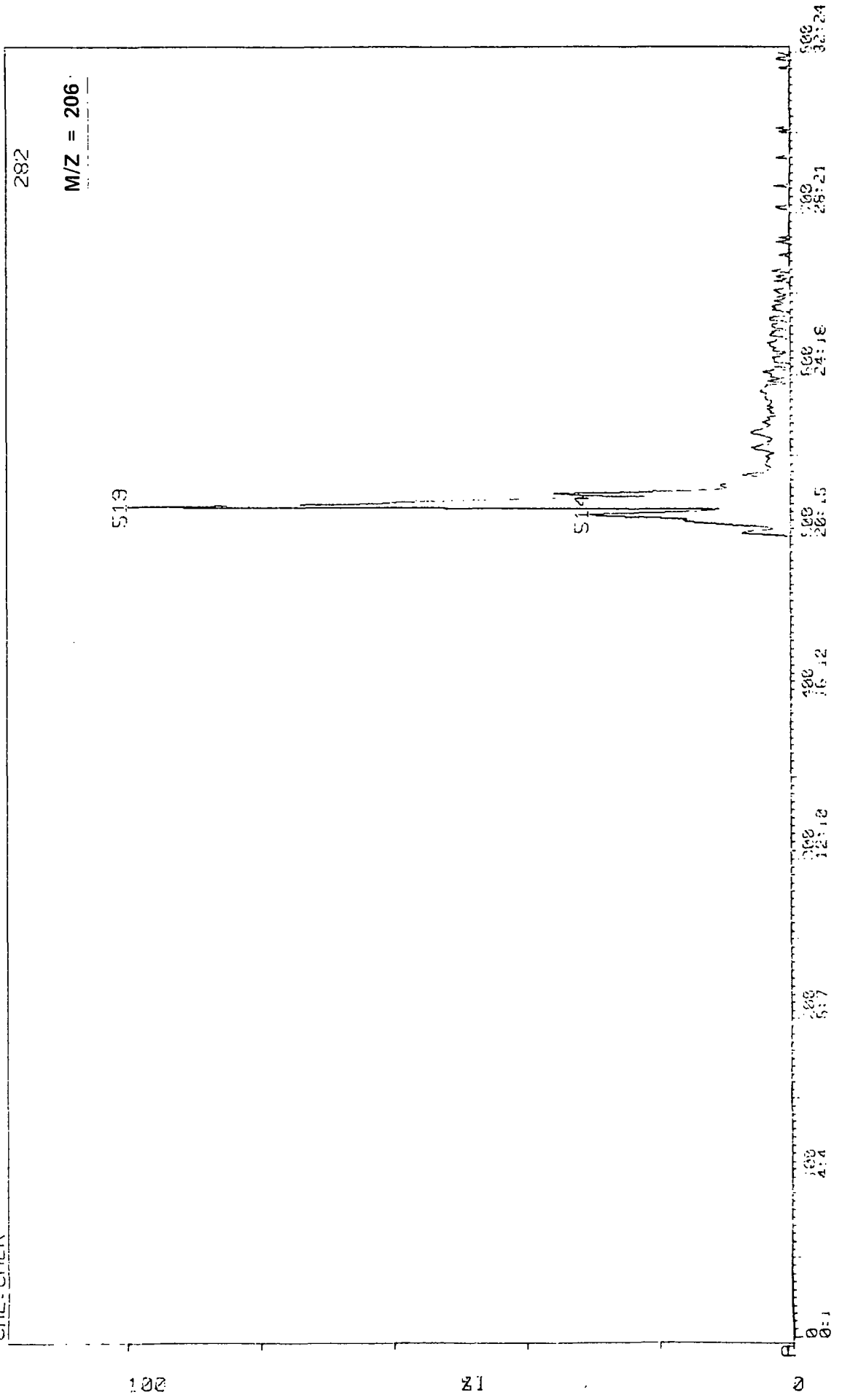
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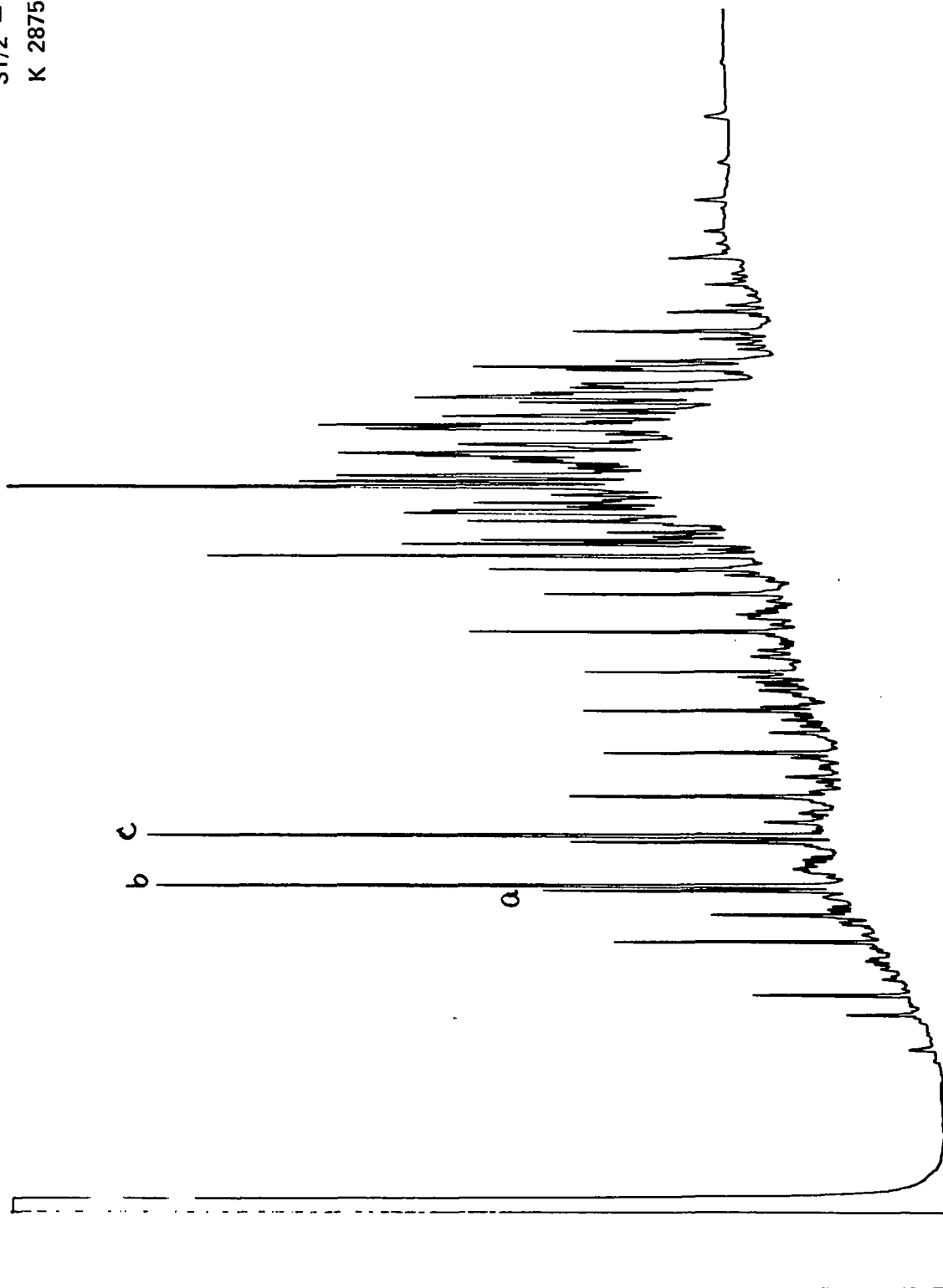
K4924A 2 - 800 K4924 AROMATIC FRACTION

28-AUG-80

A: M=206
CAL: CALK

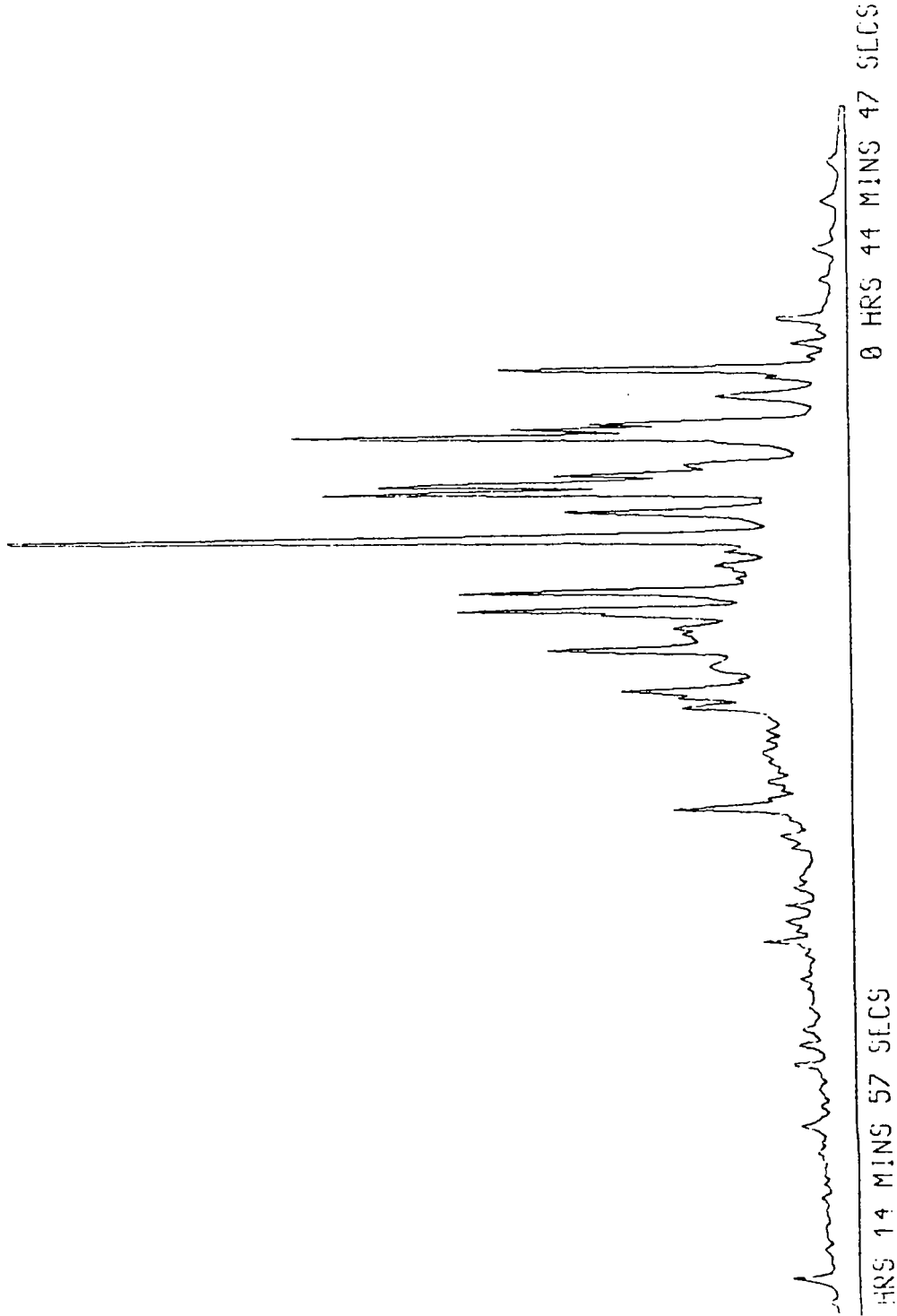


31/2 - 2 1516 m
K 2875



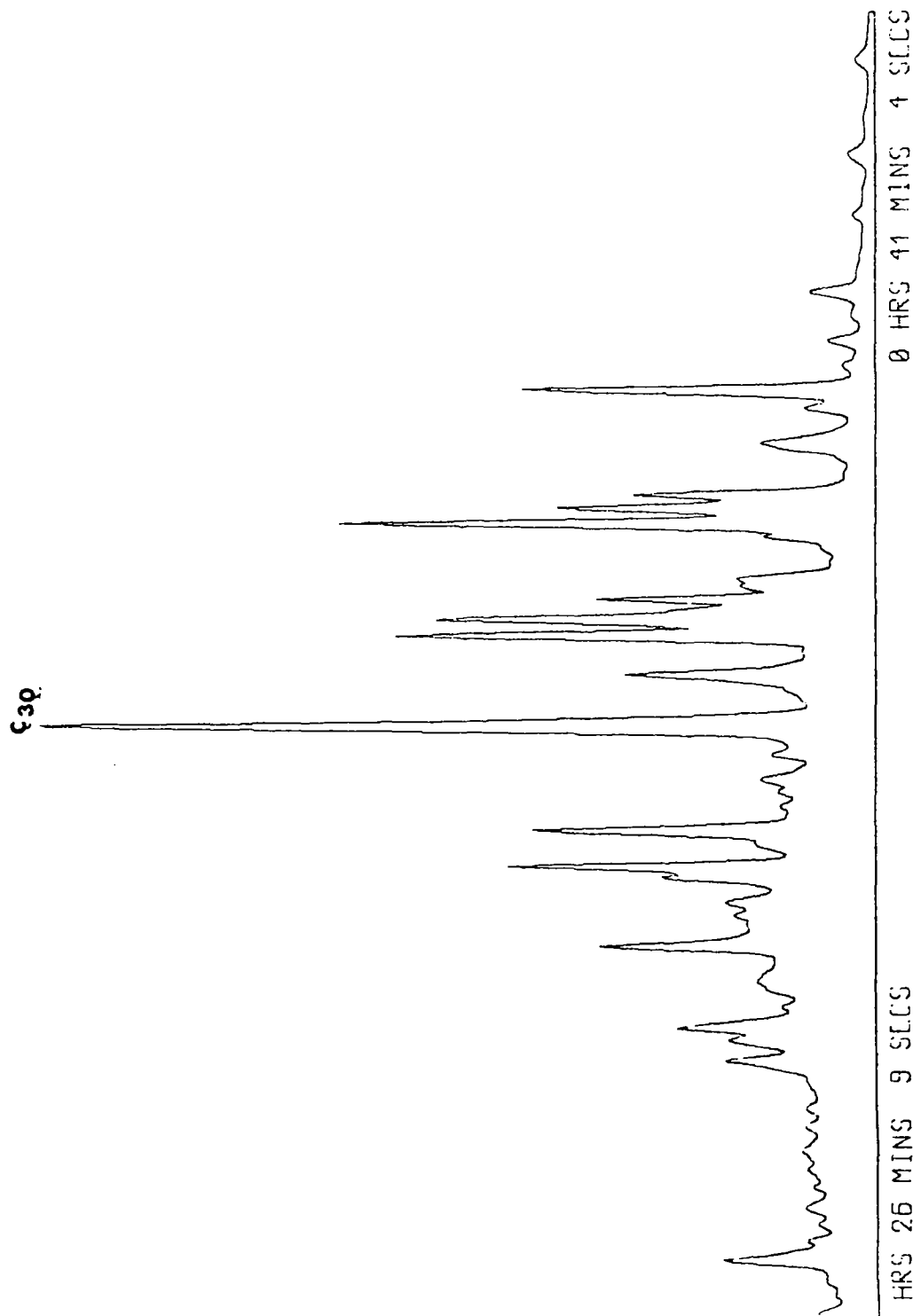
31/2-2 1516 m
K-2875
M/Z = 191

[0.0000] 2L RUN - 1
A181S 191S C199S D217S E253S F259S UNCALIBRATED.
RET. TIME HEIGHT AREA
0.15.01 18.77 130.84



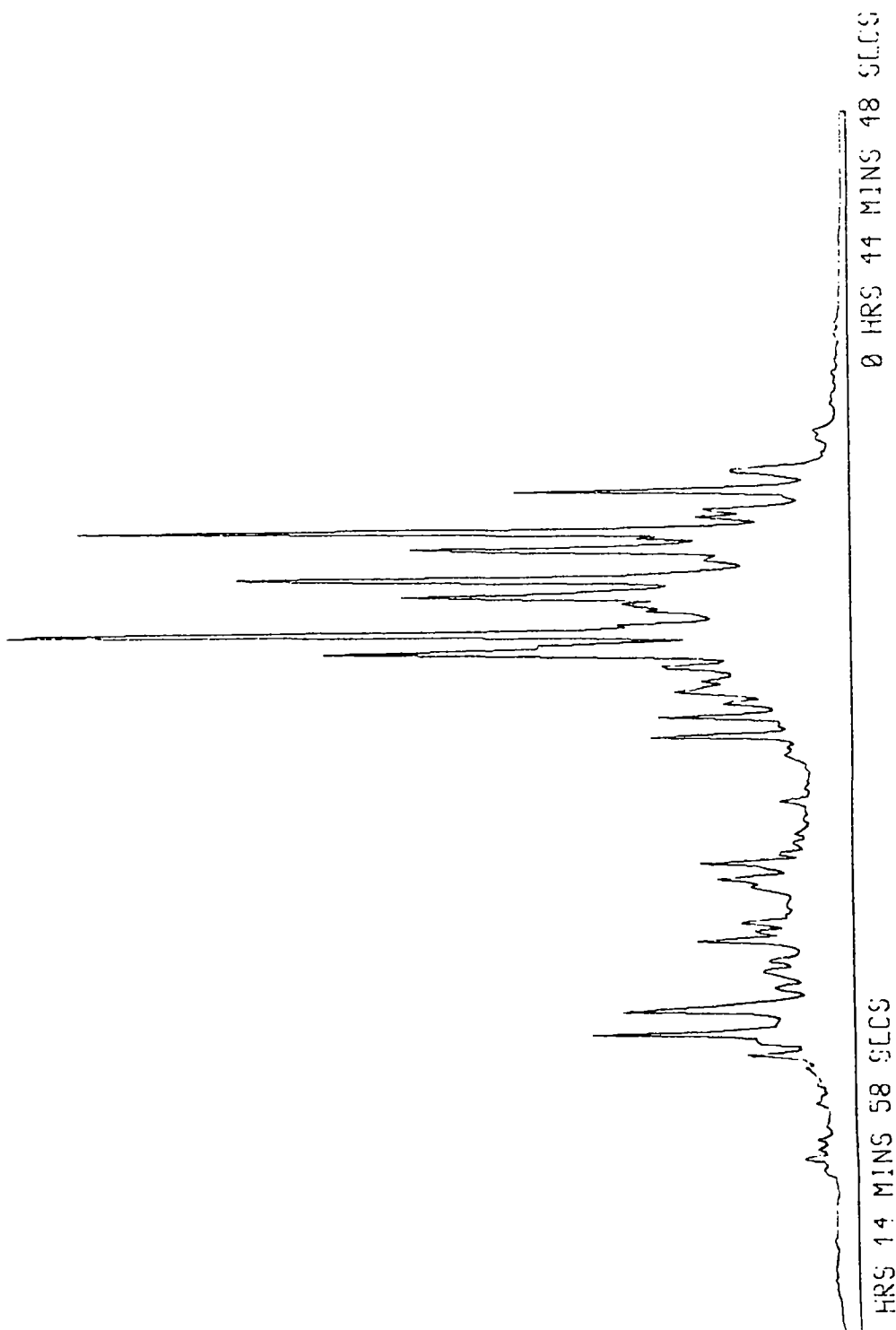
31/2-2 1516 m
K-2875
M/Z = 191

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0:25 12 49.58 243.49



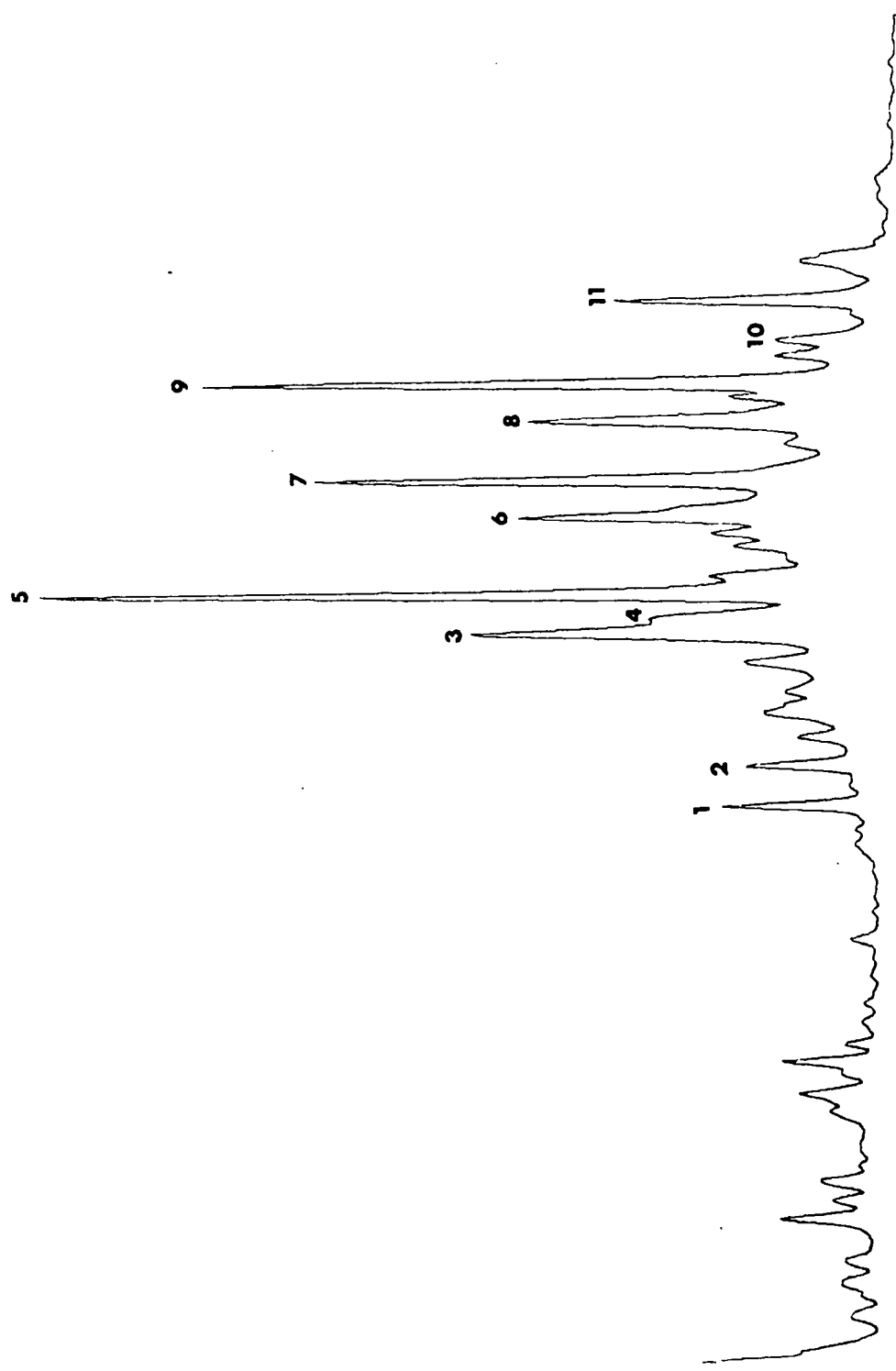
31/2-2 1516 m
K-2875
M/Z = 217

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RET. TIME HEIGHT AREA
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31/2-2 1516 m
K-2875
M/Z = 217

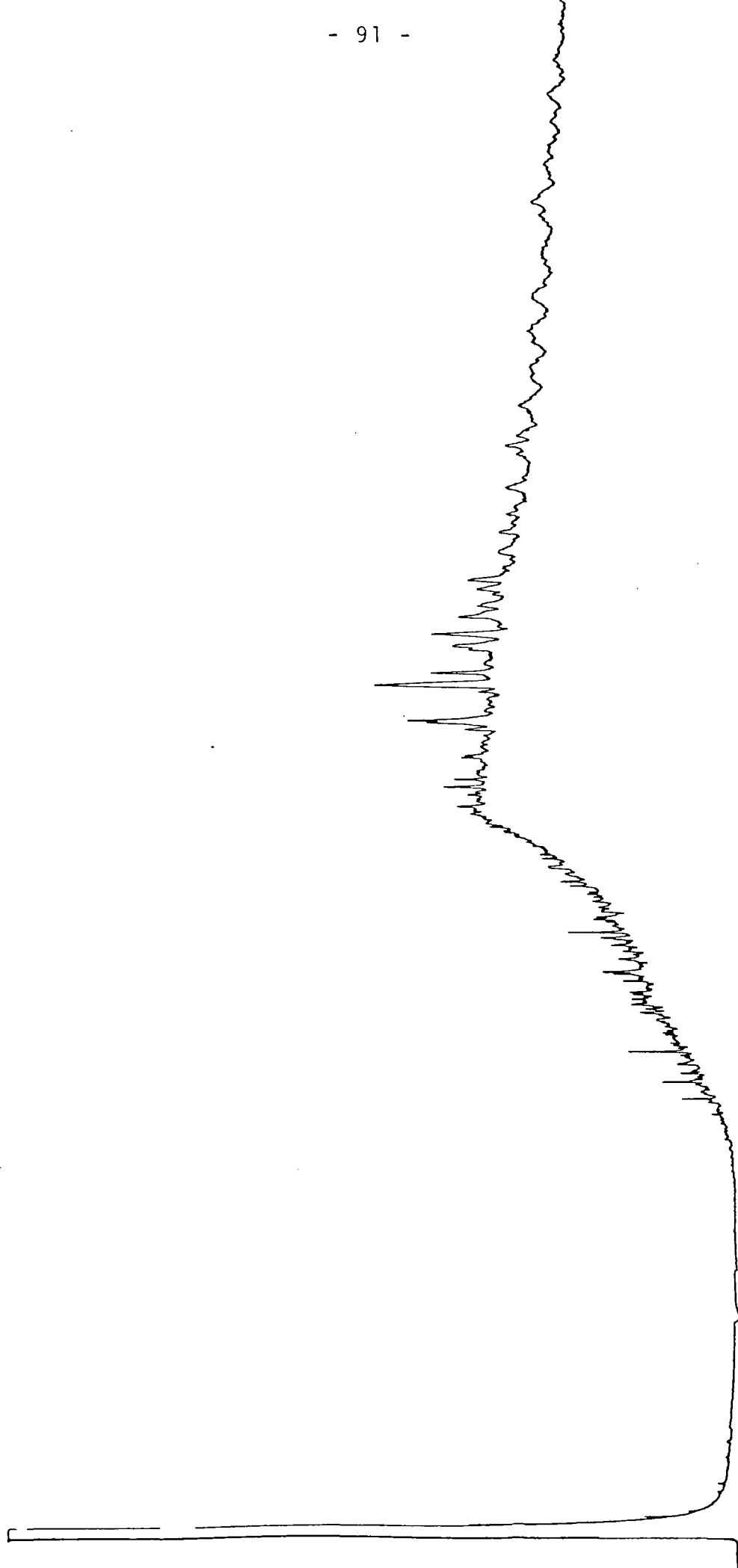
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0:22:28 46.76 233.76



HRS 22 MINS 25 SECS

0 HRS 37 MINS 20 SECS

31/2-2 1516 m AROMATIC

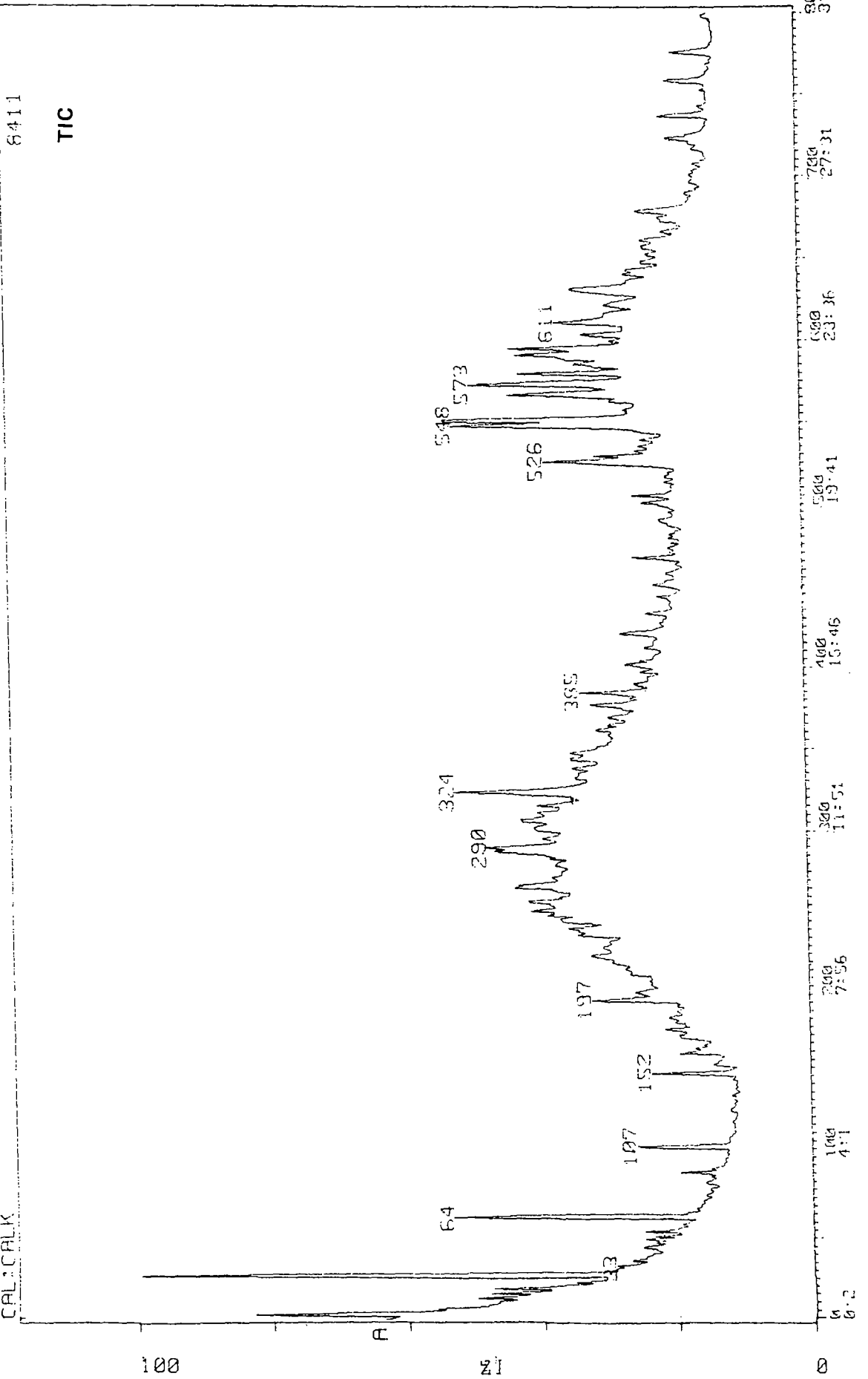


15-SEP-80

2875FC 0-874 AROMATICS 2875 FDC

A:TIC B:M=253 C:M=339 D:M=365

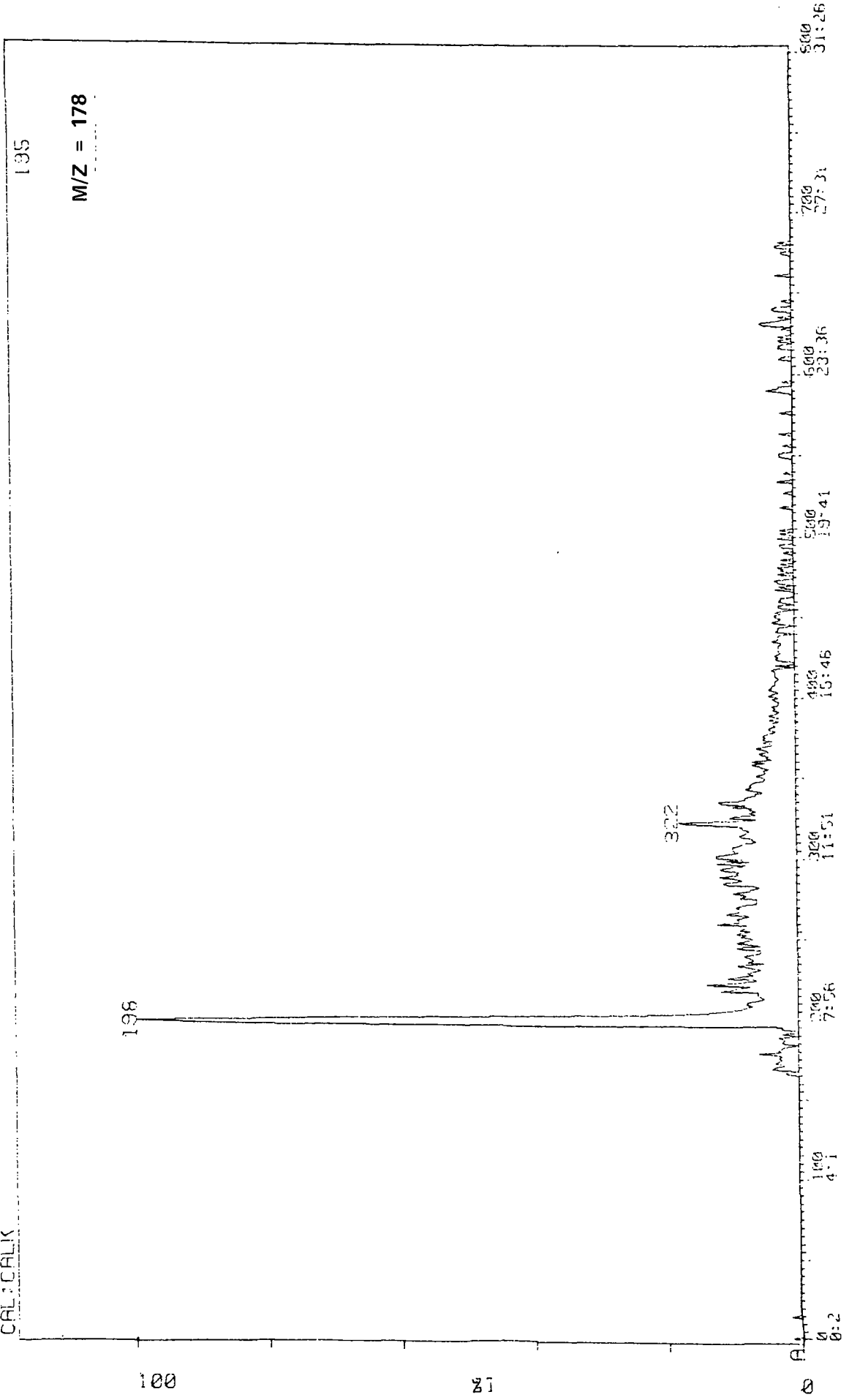
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15-SEP-80

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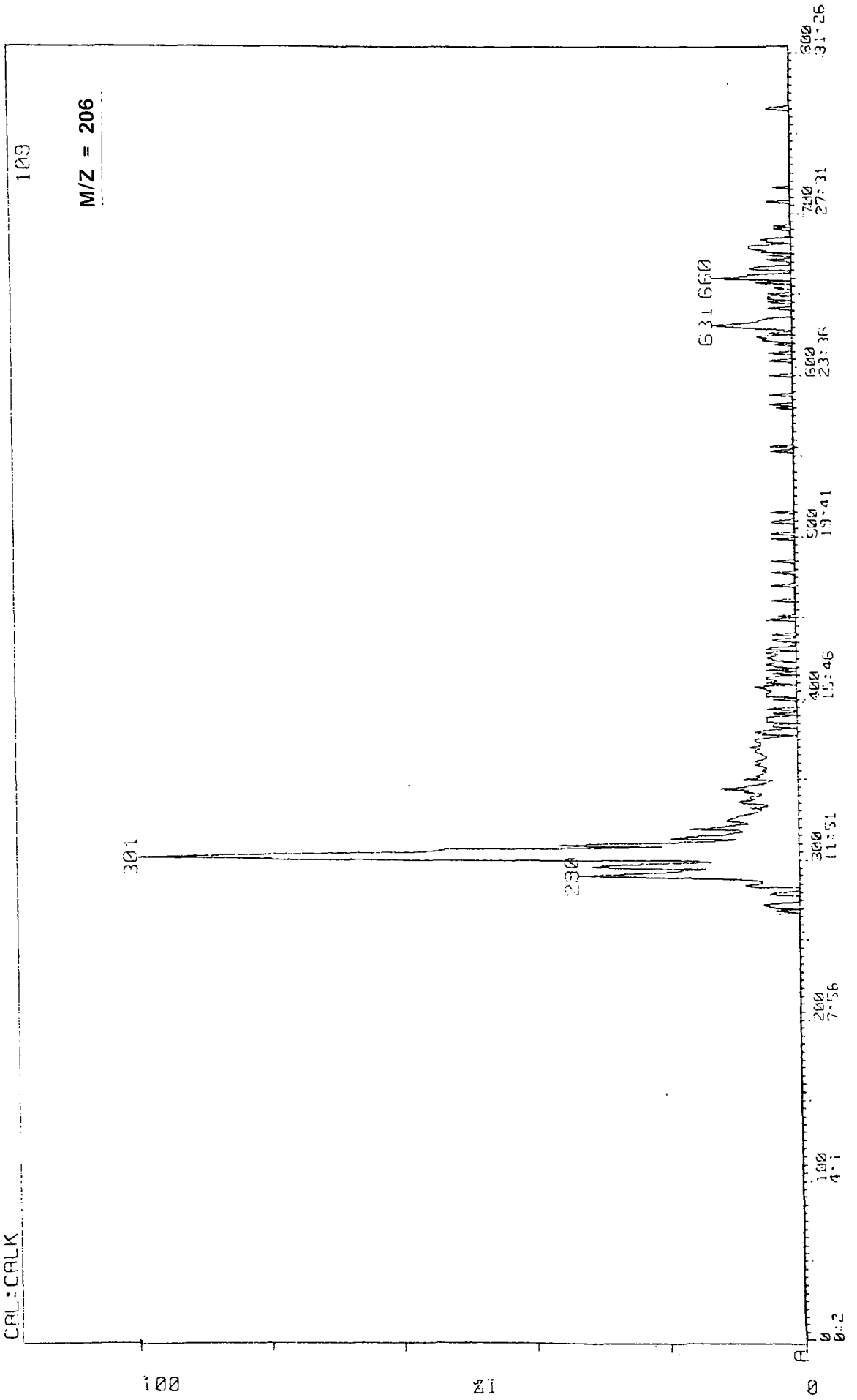
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15-SEP-80

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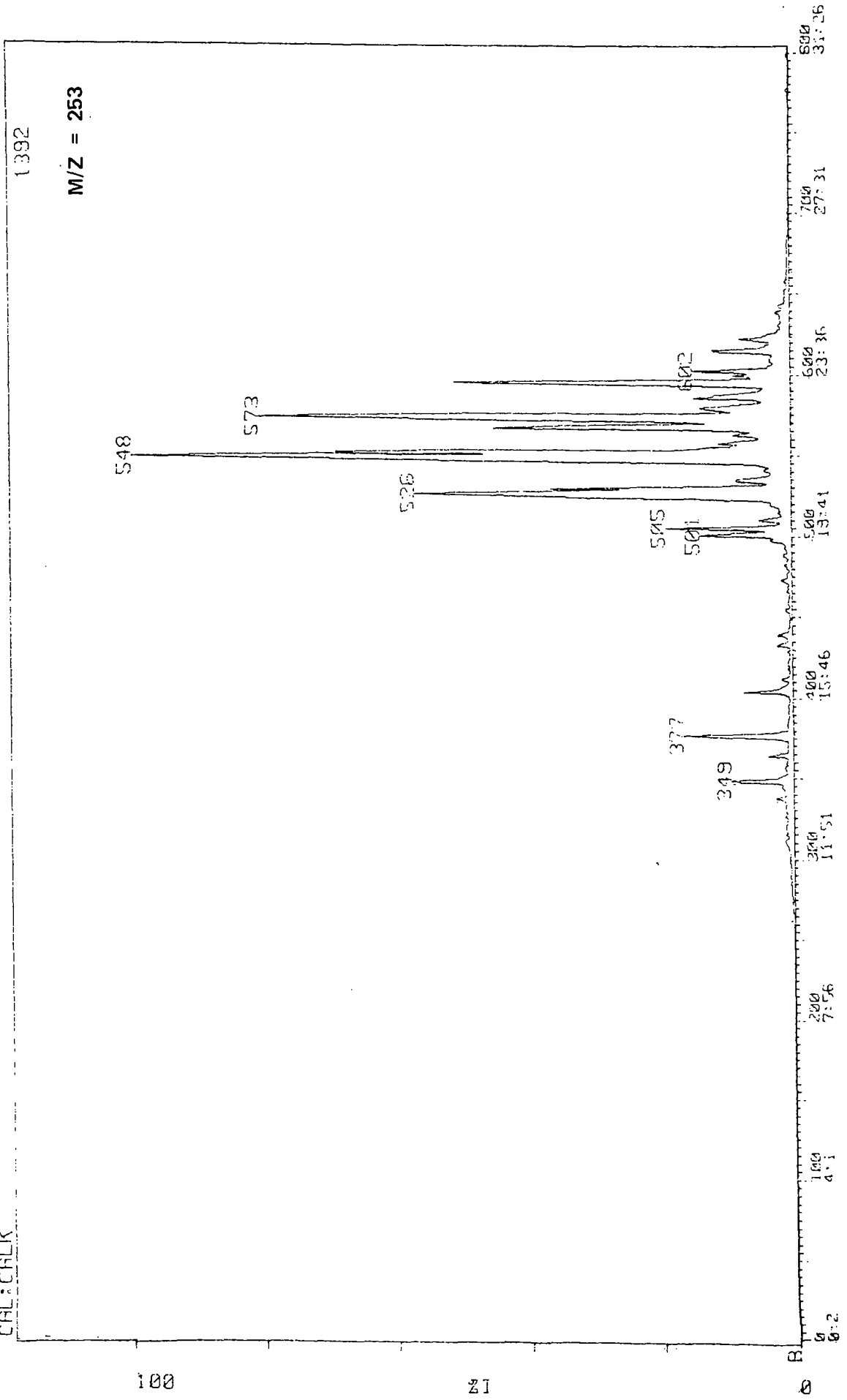
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15-SEP-80

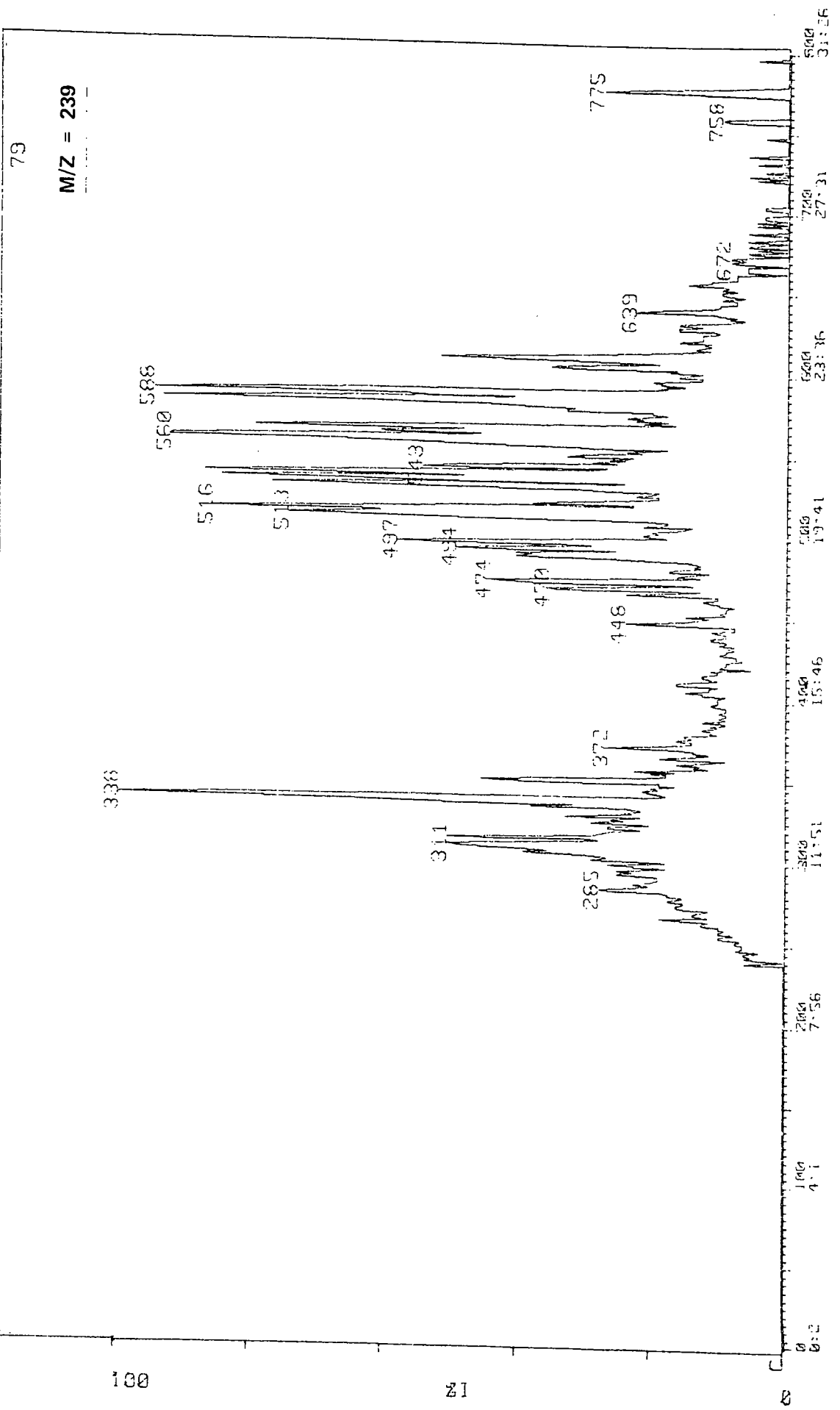
2875FC 0 - 874 AROMATICS 2875 FDC

A: TIC B: M=253 C: M=239 D: M=365
CAL: CALK



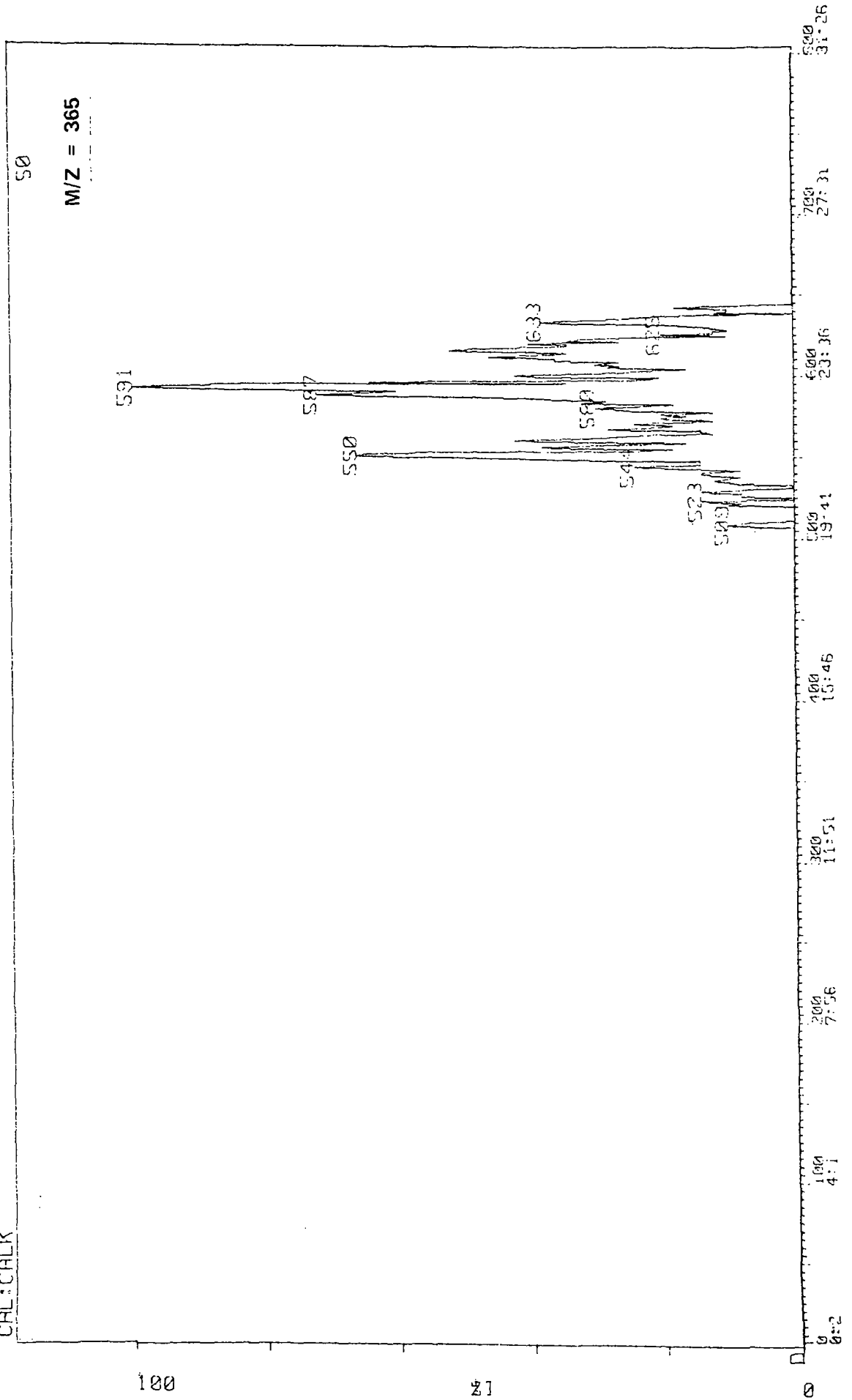
15-SEP-80

2875FC0-874 AROMATICS 2875 FDC
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CAL: CALK



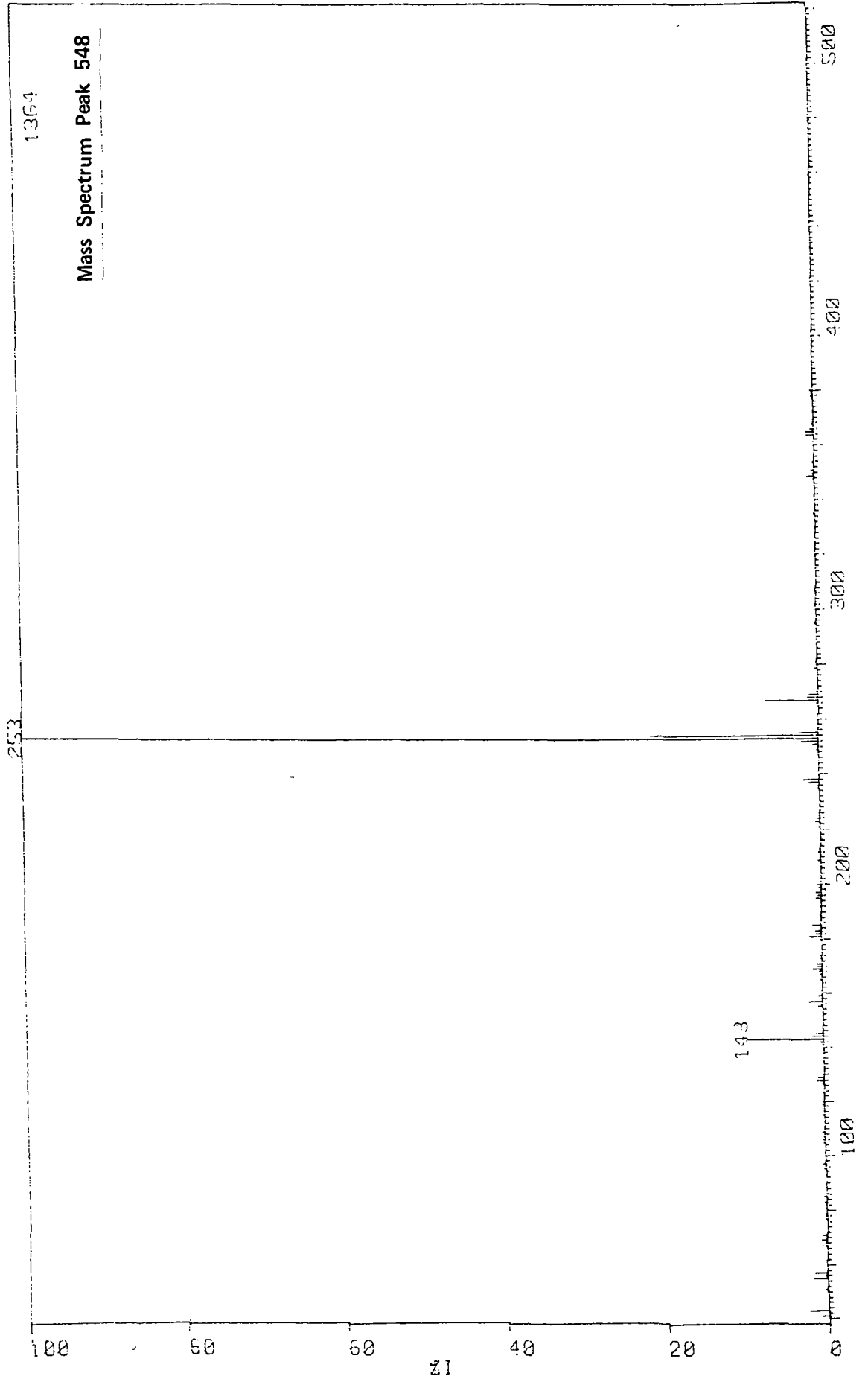
15-SEP-80

2875FC0-874 AROMATICS 2875 FDC
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CAL:CALK



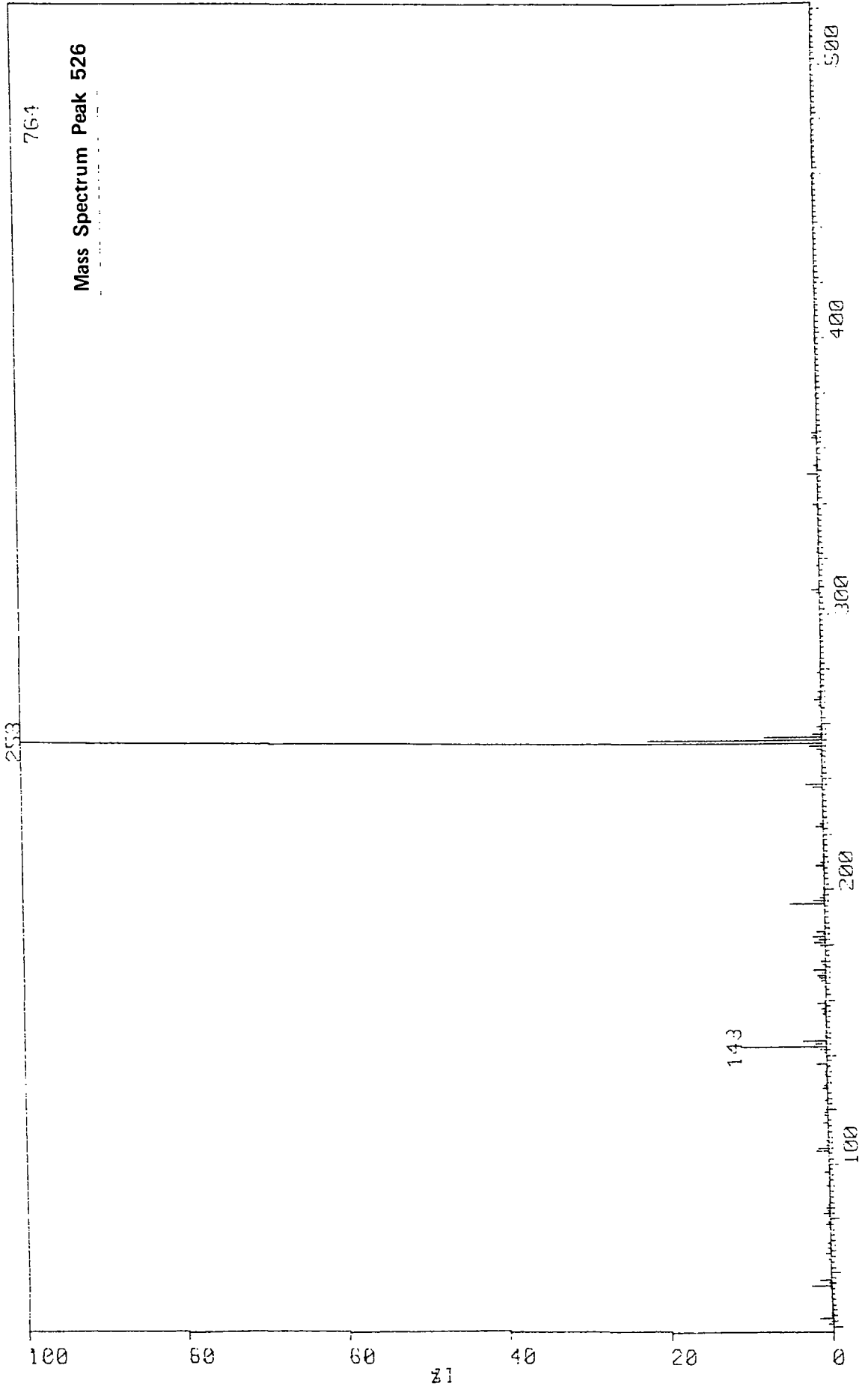
15-SEP-80

2875FC 548 AROMATICS 2875 FDC
CAL:CALK



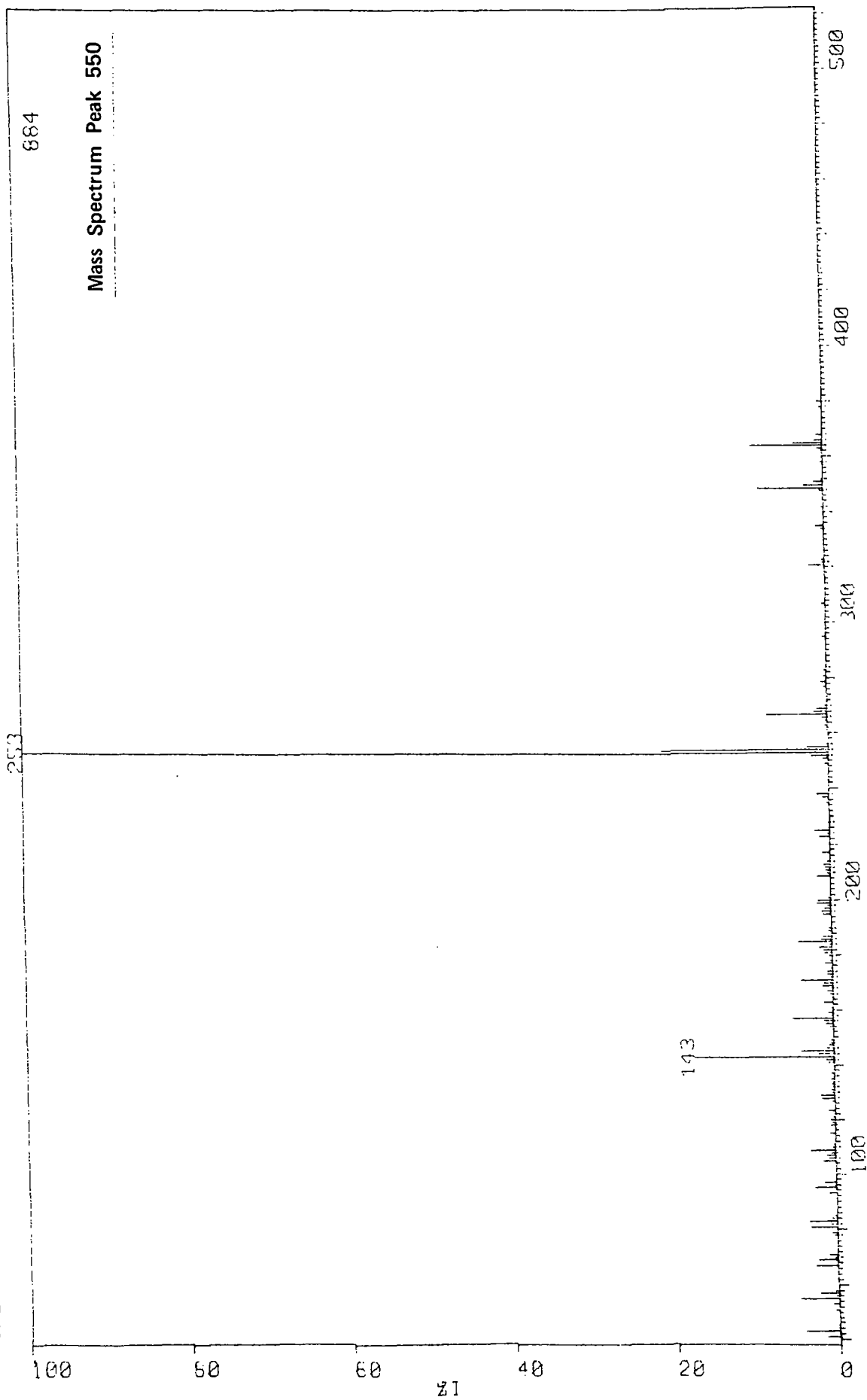
15-SEP-80

2875FC 526 AROMATICS 2875 FDC
CAL:CALK



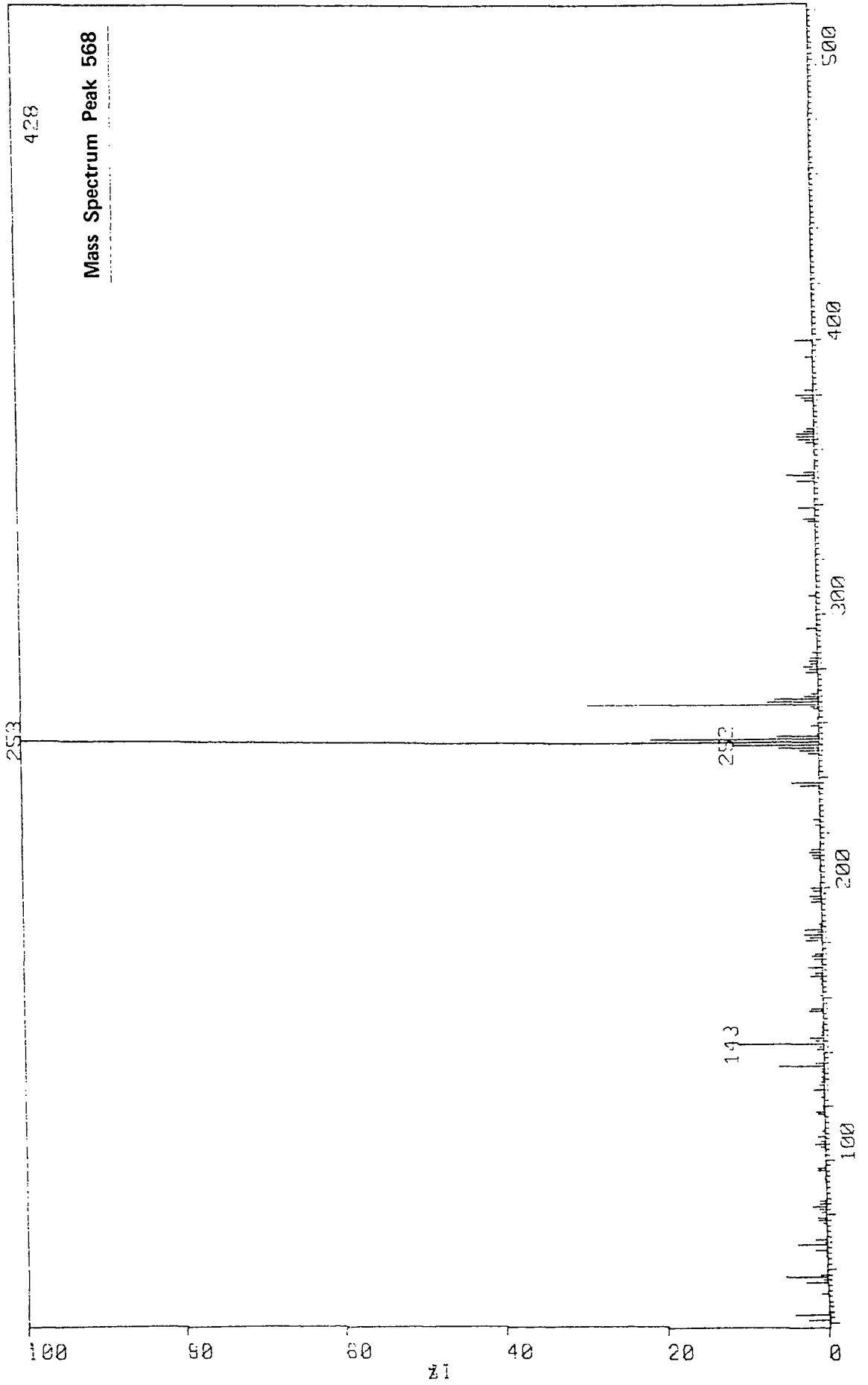
15-SEP-80

2875FC 550 AROMATICS 2875 FDC
CAL:CALK



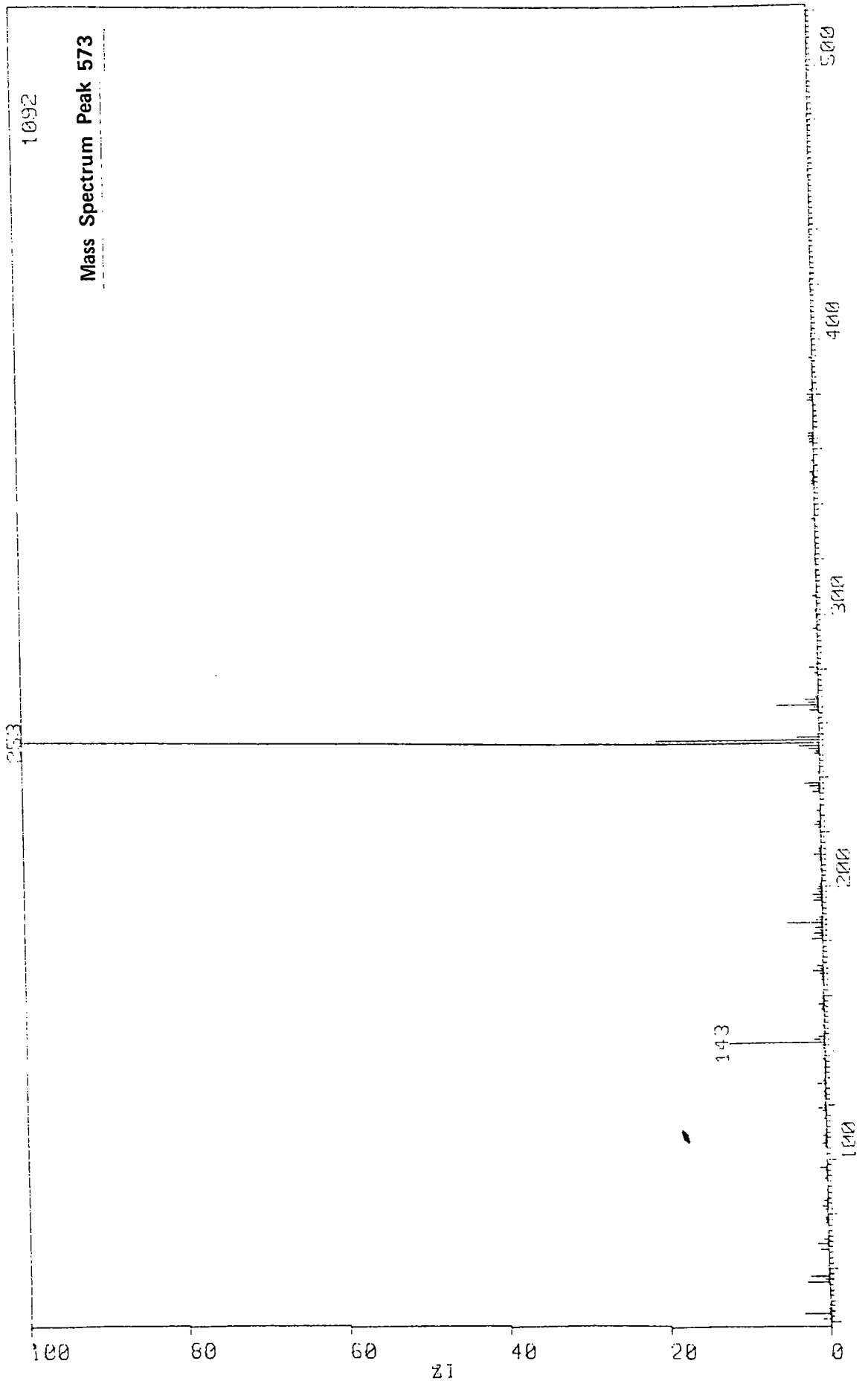
15-SEP-80

2875FC 568 AROMATICS 2875 FDC
CAL:CALK



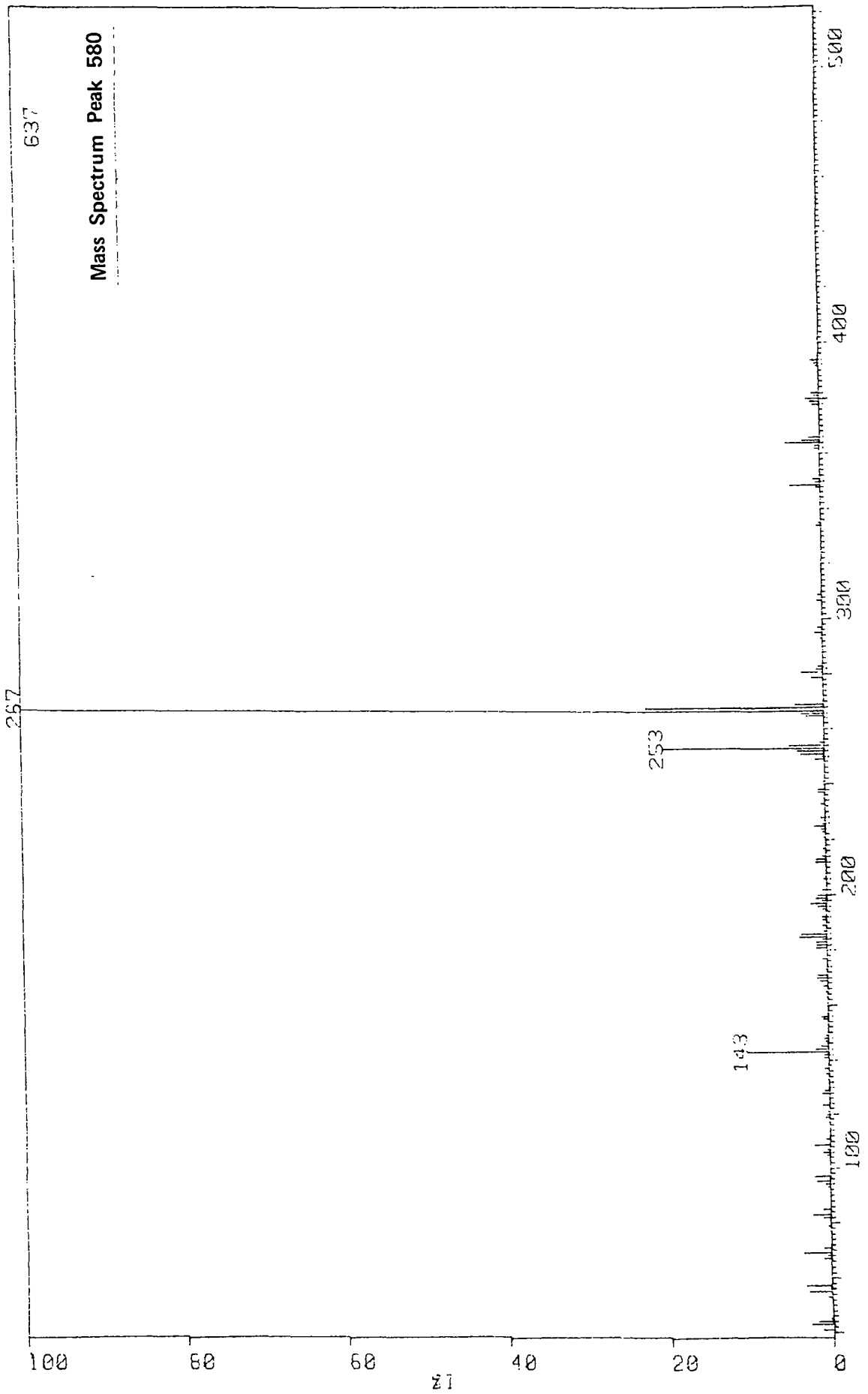
15-SEP-80

2875FC 573 AROMATICS 2875 FDC
CAL:CALK



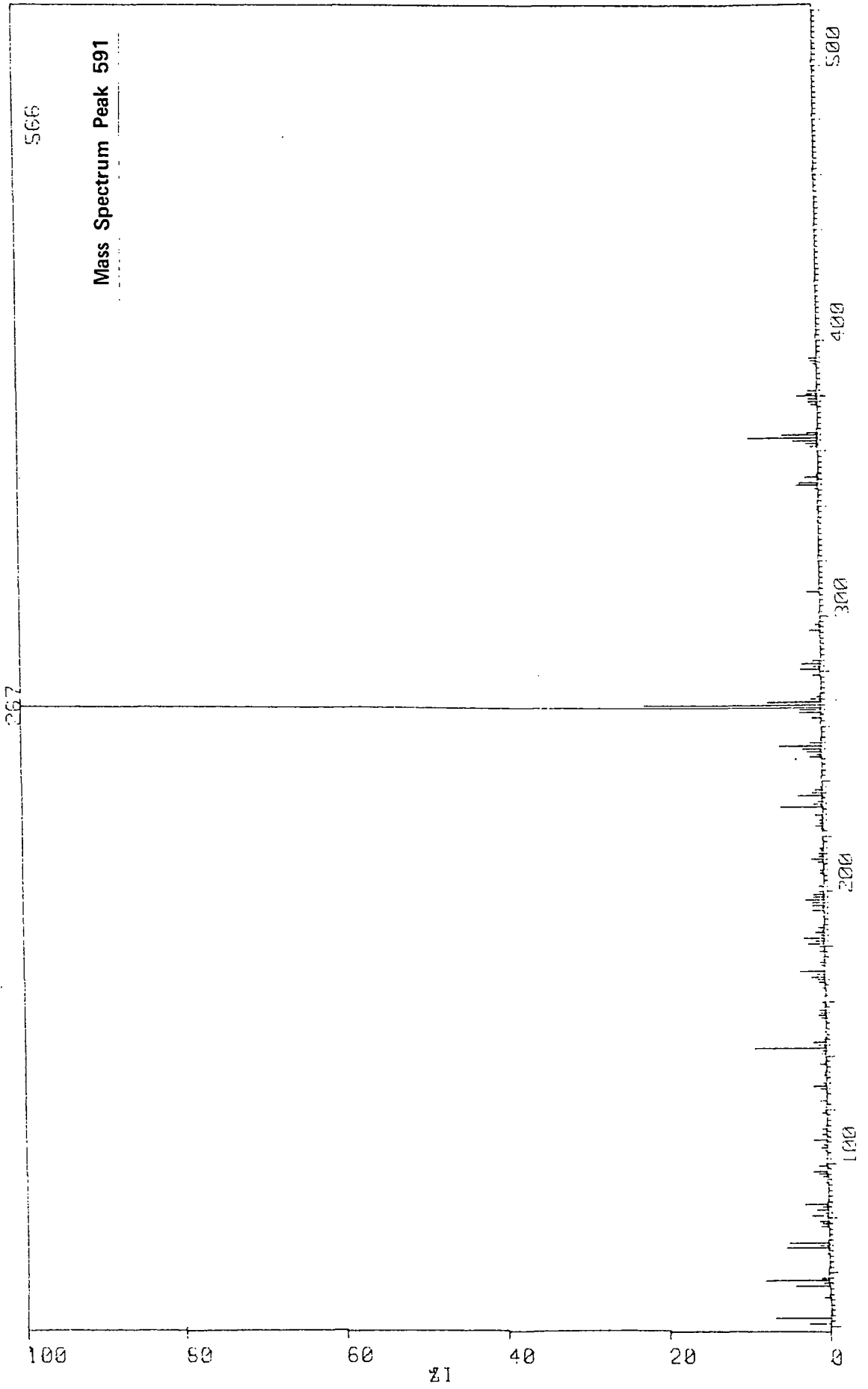
15-SEP-80

2875FC 580 AROMATICS 2875 FDC
CAL:CALK



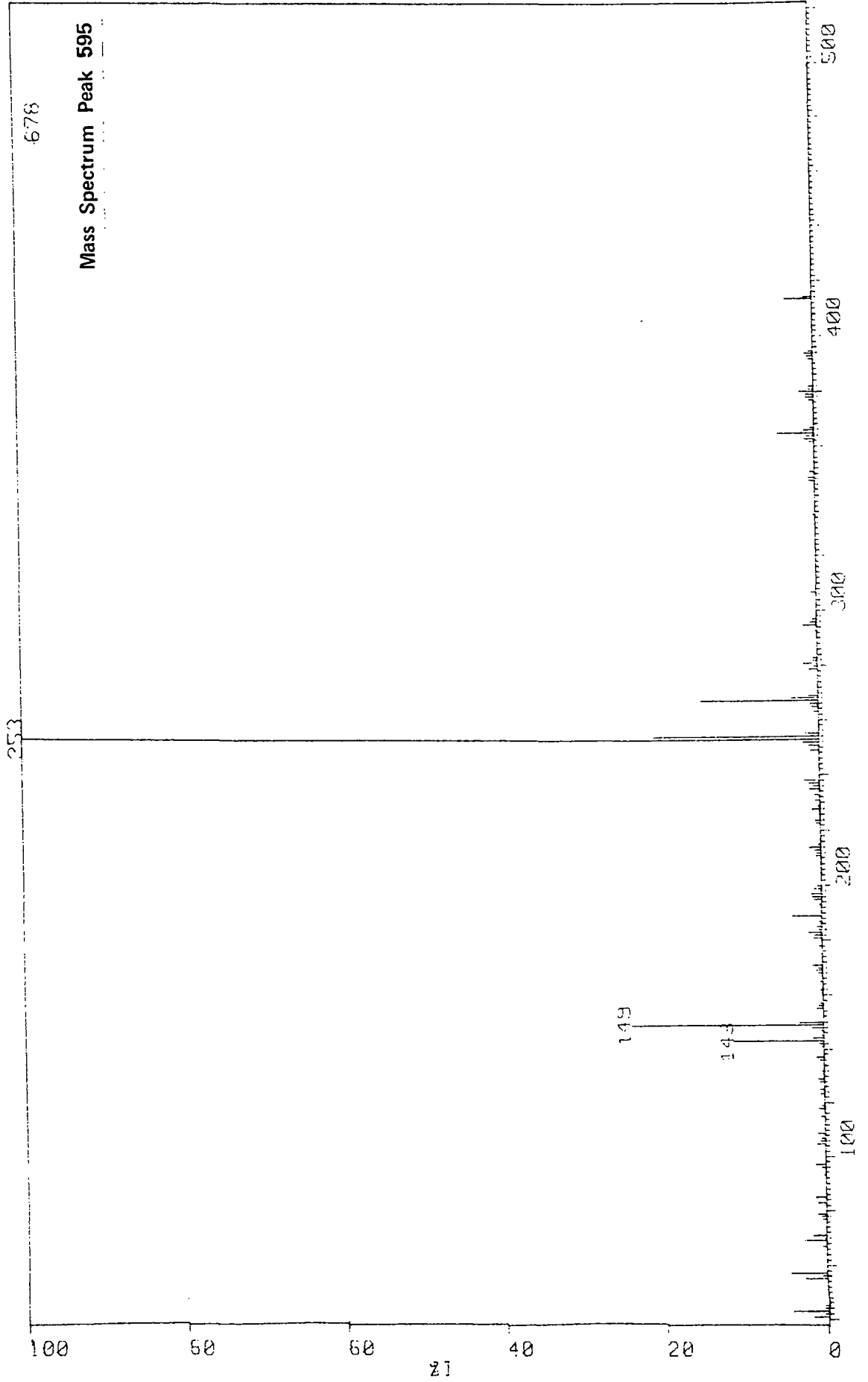
15-SEP-80

2875FC 591 AROMATICS 2875 FDC
CALC



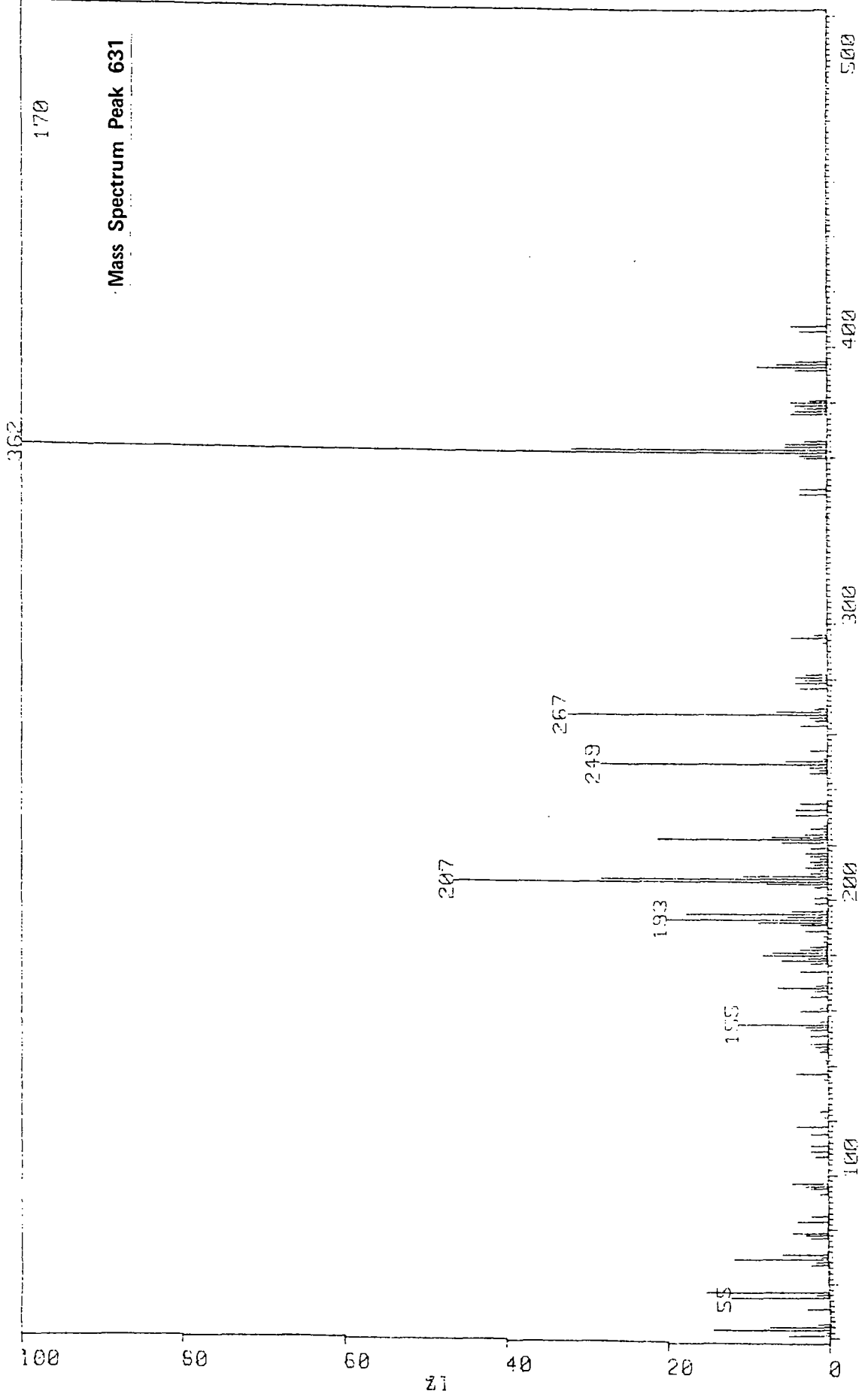
15-SEP-80

2875FC 595 AROMATICS 2875 FDC
CAL:CALK



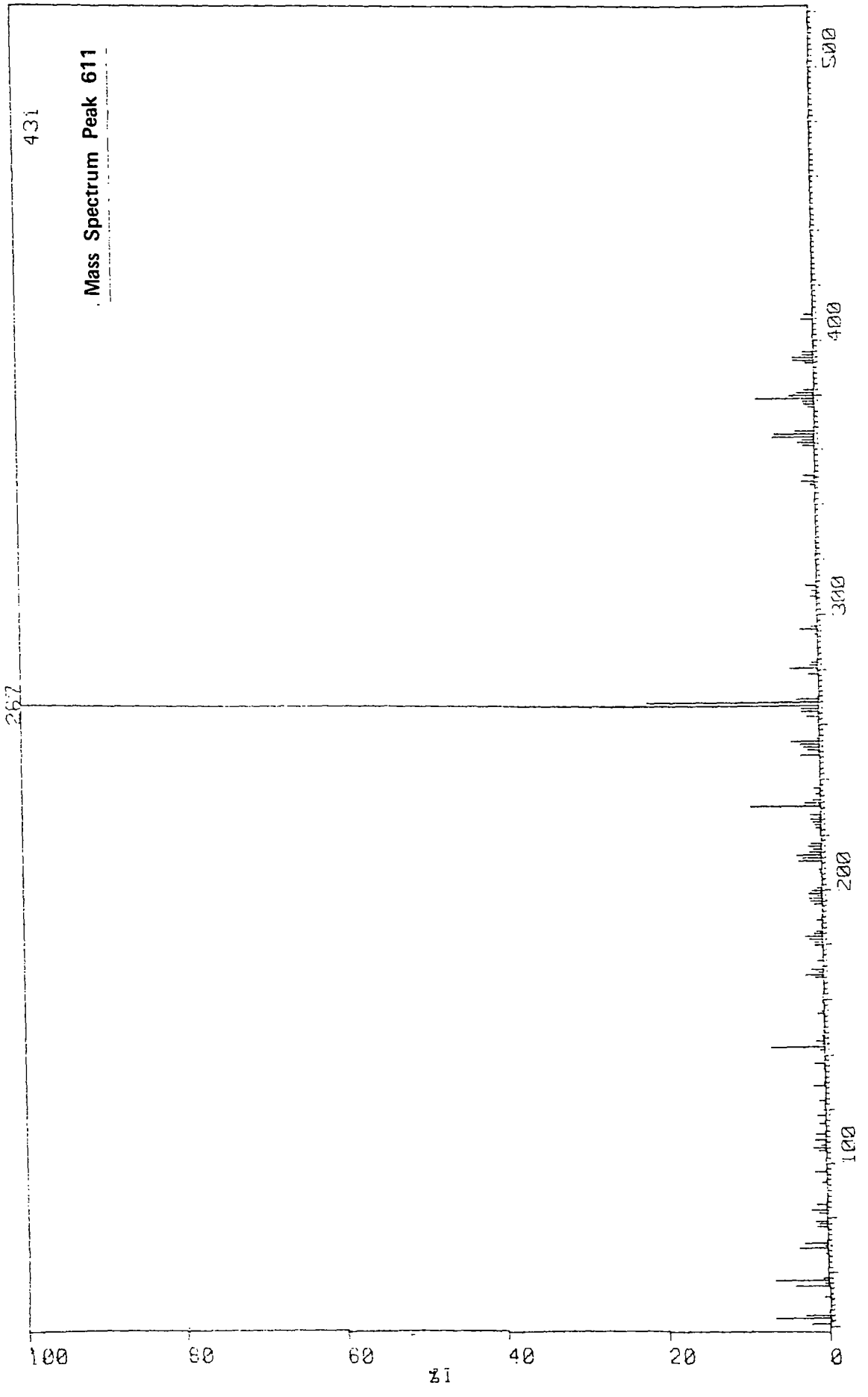
2875FC 631 ARDMATICS 2875 FDC
CAL:CALK

15-SEP-80



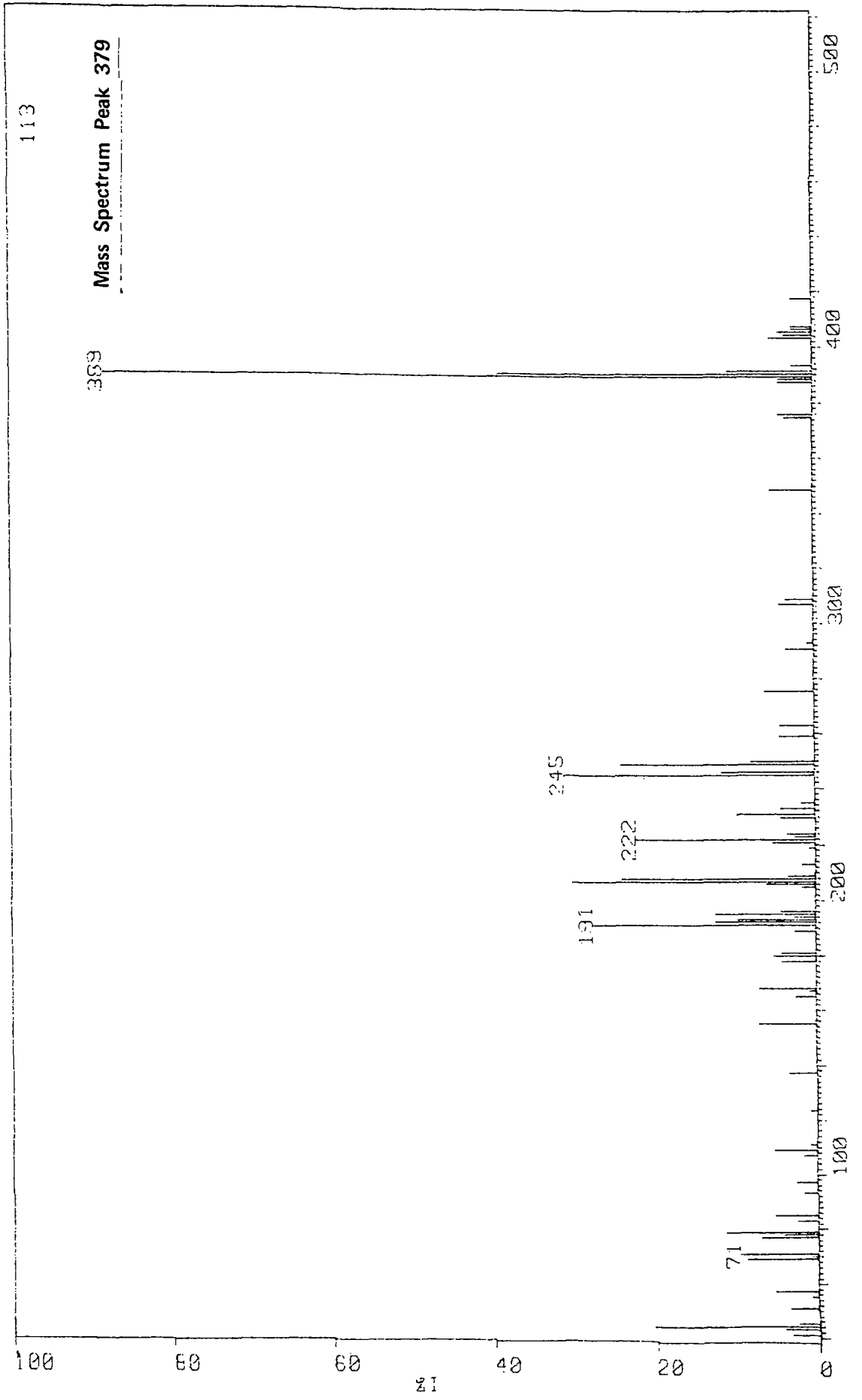
15-SEP-80

2875FC 611 AROMATICS 2875 FDC
CAL:CALK



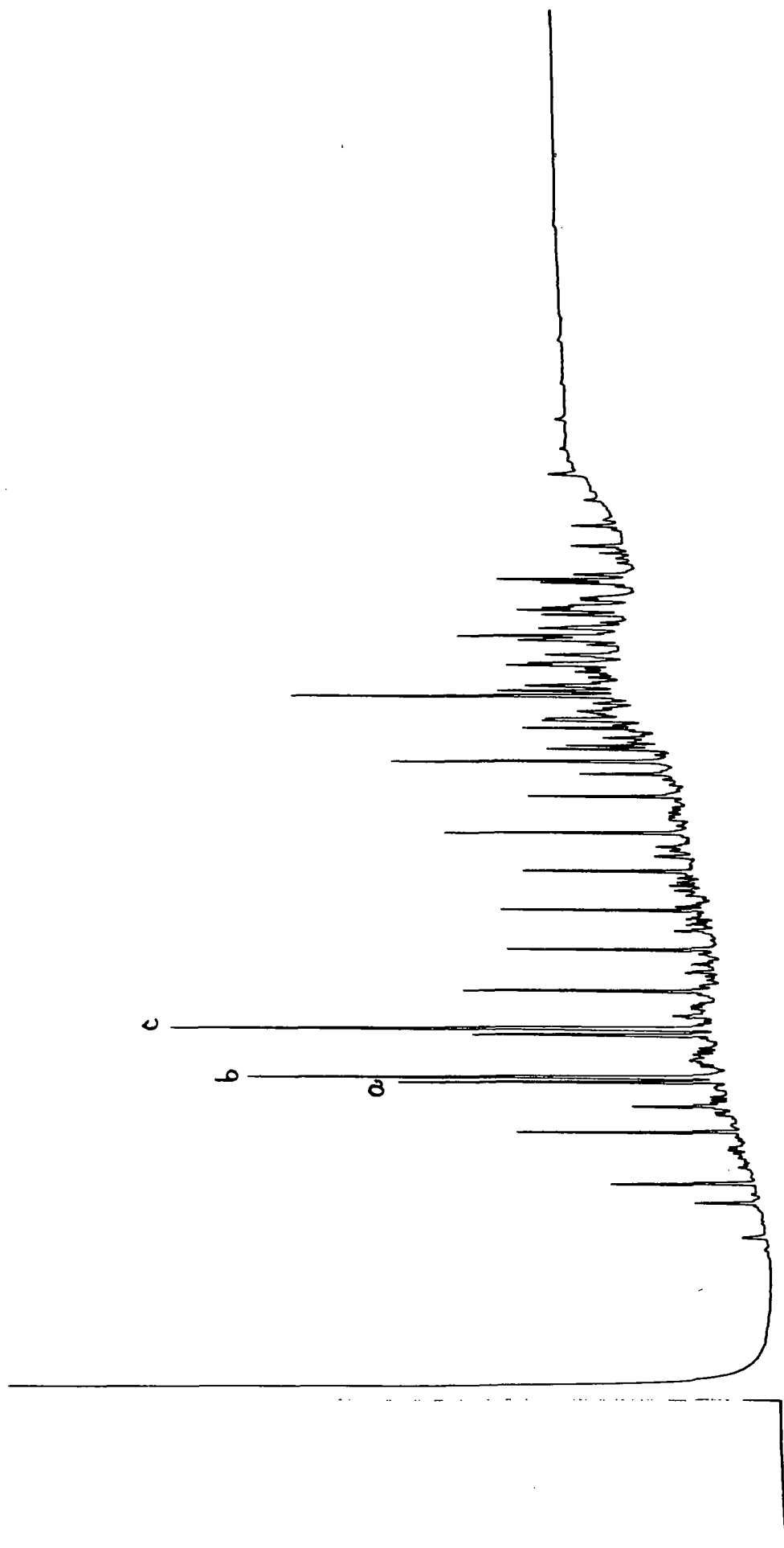
15-SEP-80

2875FC 679 ARUMATICS 2875 FDC
CAL:CALIK



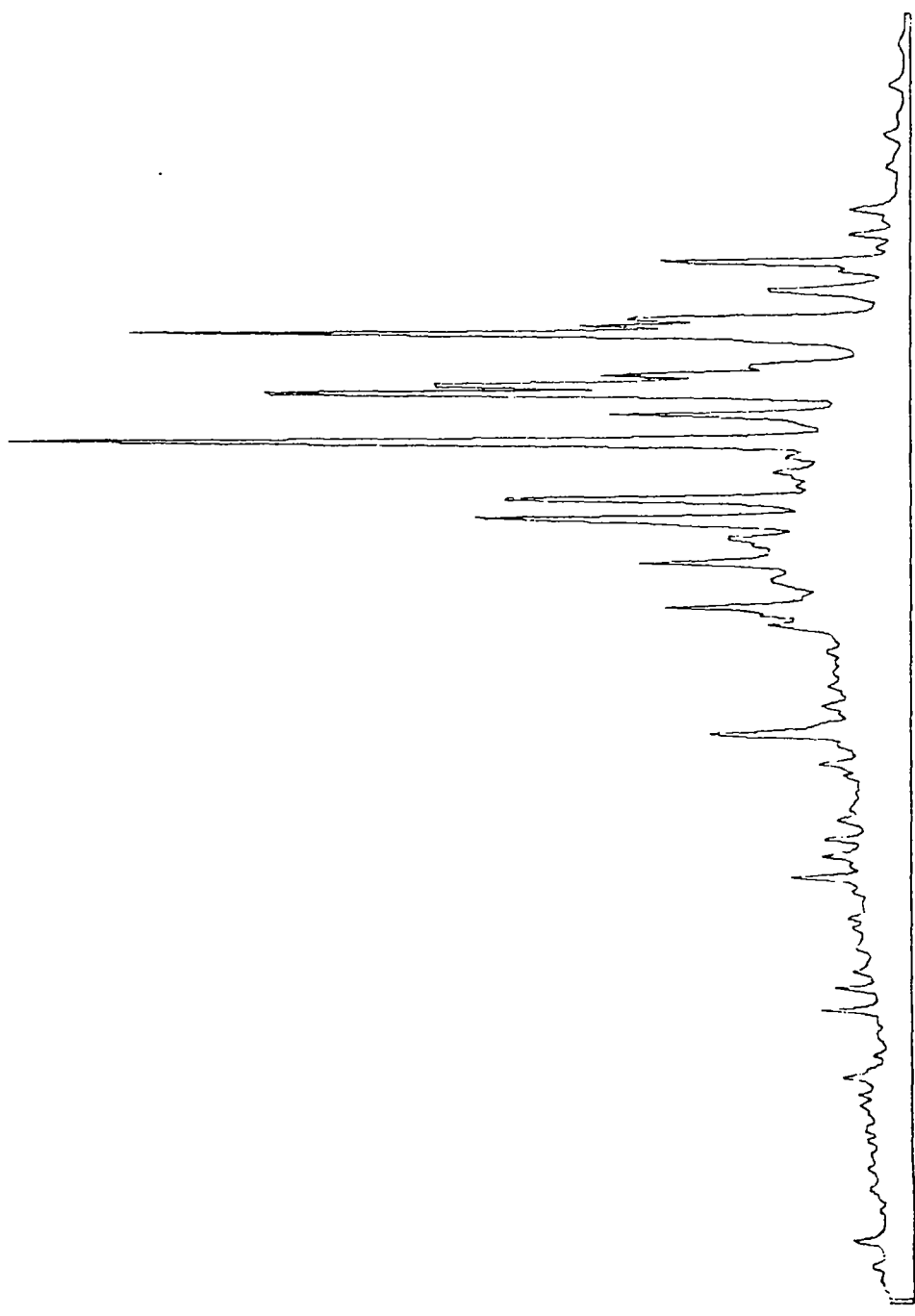
31/2 - 2 1537 m

K 2876



31/2-2 1537 m
M/Z = 191

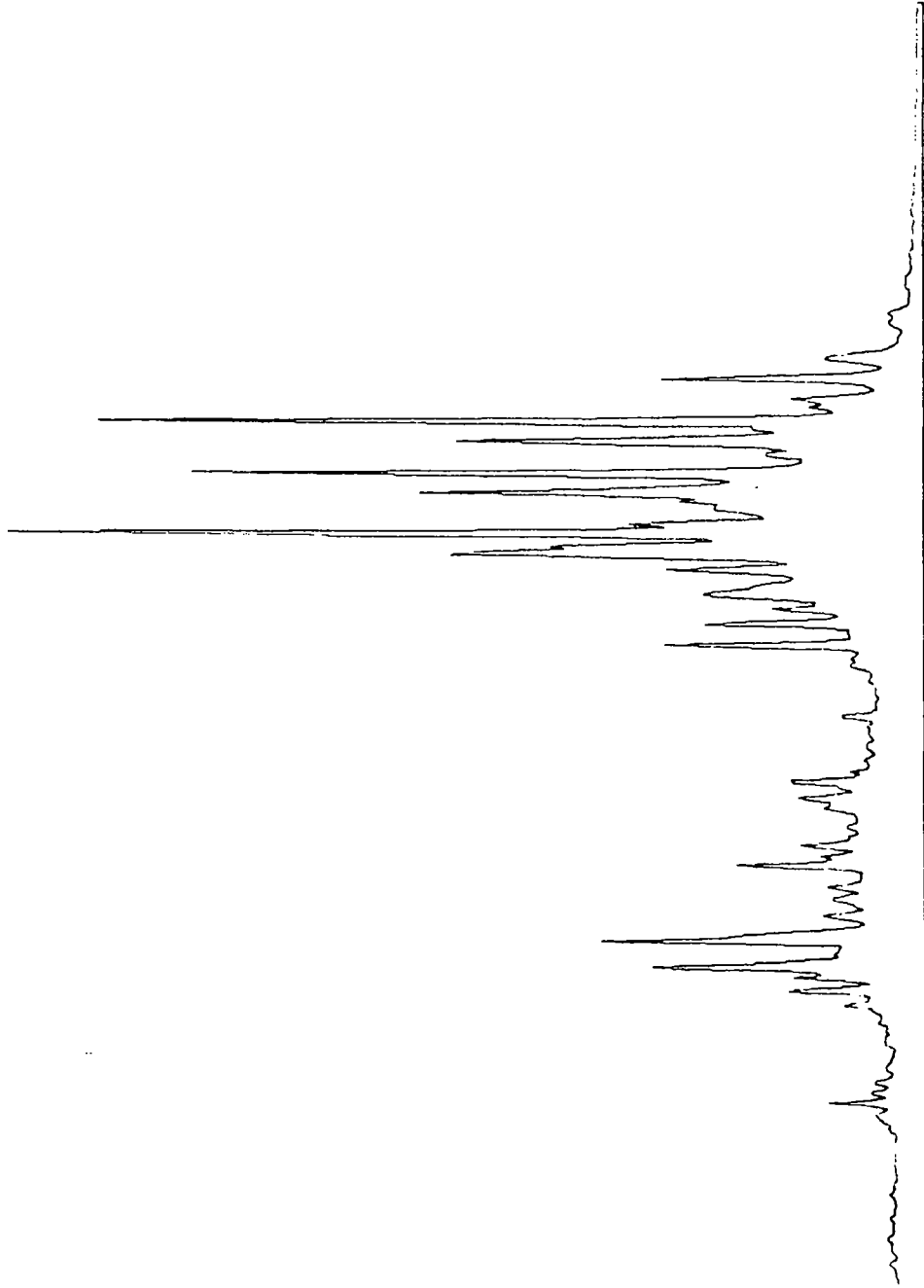
0.0000] 2L RUN - 1 2876 SATURATED SAMPLE 2
A1815 1915 C1990 D2170 [2530 F2590
RETN. TIME HEIGHT AREA UNCALIBRATED.
0'15'05 14.15 144.27



0 HRS 14 MINS 57 SECS
0 HRS 14 MINS 47 SECS

31/2-2 1537 m
M/Z = 217

[0.0000] .2L RUN - 1 2876 SATURATED SAMPLE 2
A181S 0191S C199S #217S L253S F259S
ETN.TIME HEIGHT AREA UNCALIBRATED.
0:15:05 14.15 144.27

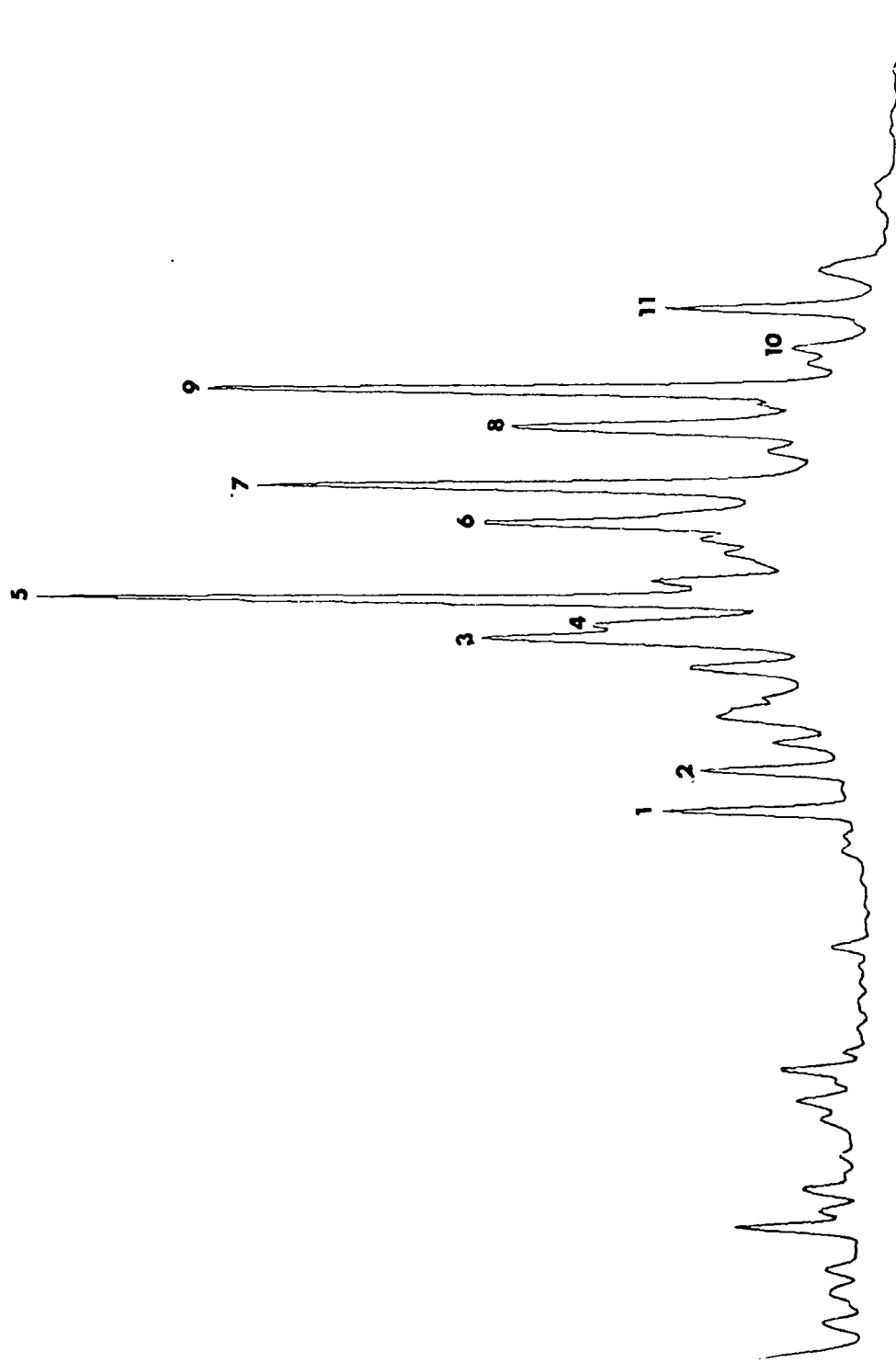


HRS 14 MINS 58 SECS

0 HRS 44 MINS 48 SECS

31/2-2 1537 m
M/Z = 217

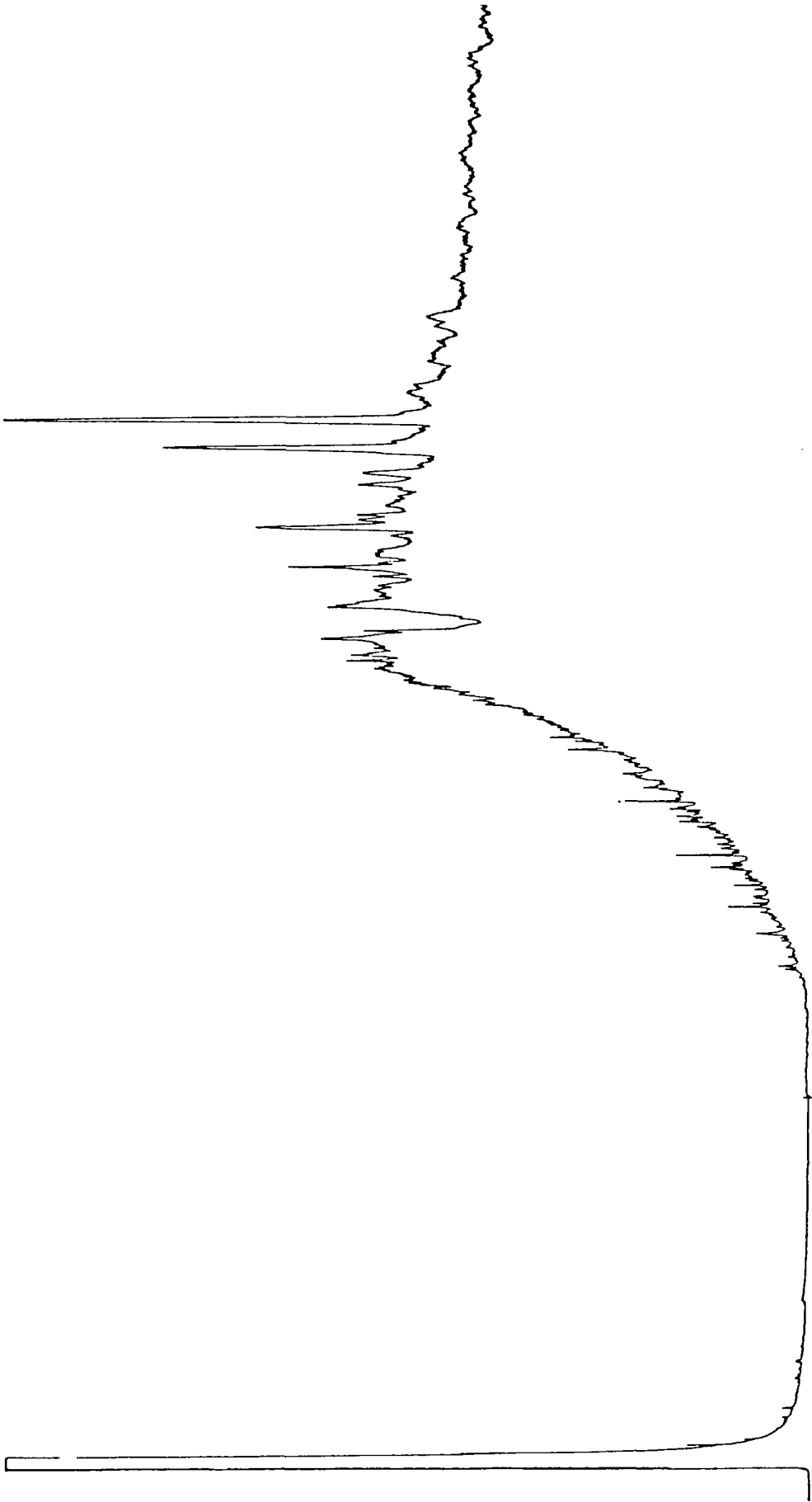
[0.0000] .2L RUN - 1 2876 SATURATES SAMPLE 2
A181S B191S C199S E217S E253S F259S
ETN.TIME HEIGHT AREA UNCALIBRATED.
0:22:28 159.84 1073.02



HRS 22 MINS 25 SECS

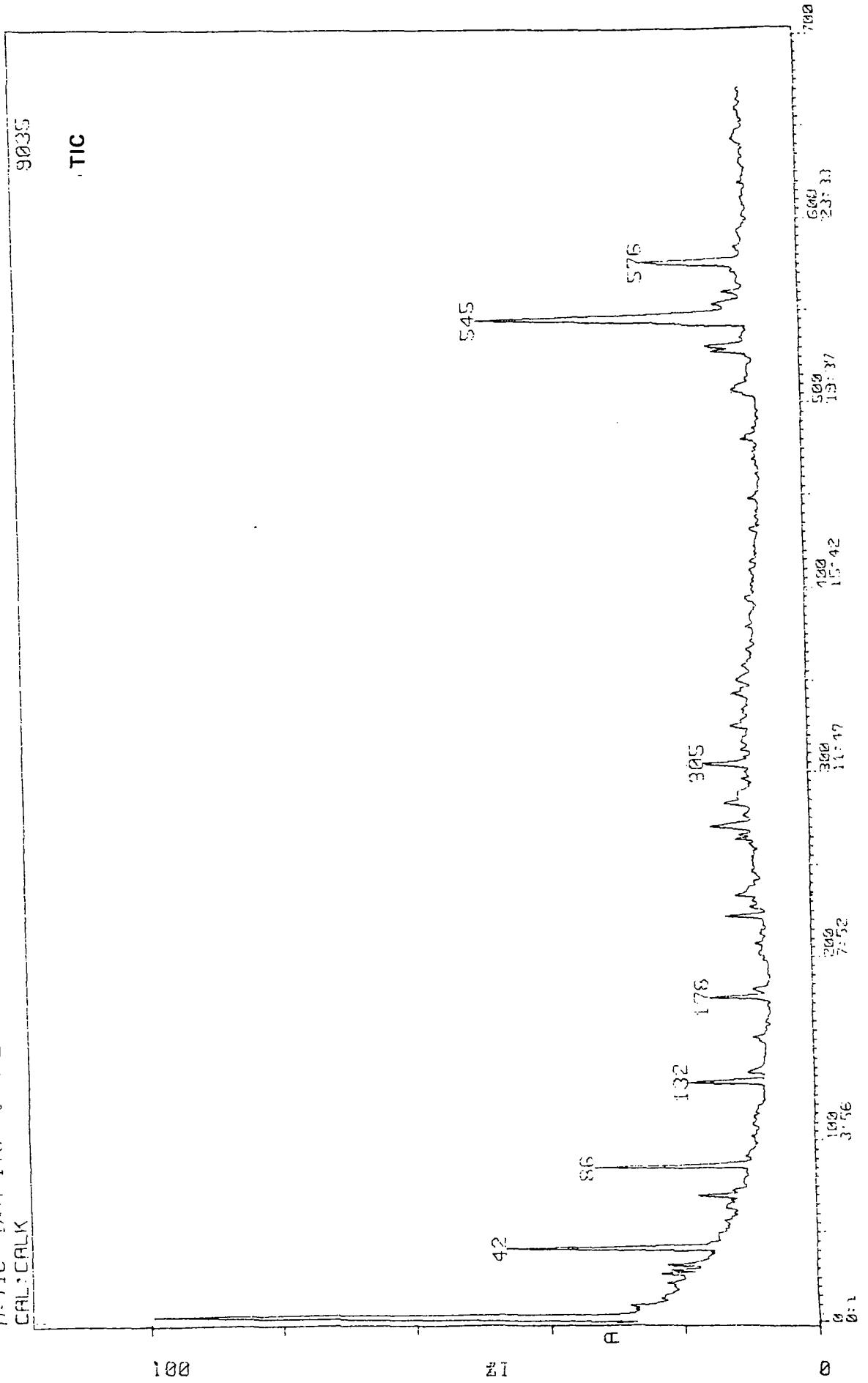
0 HRS 37 MINS 20 SECS

31/2-2 1537 m AROMATIC



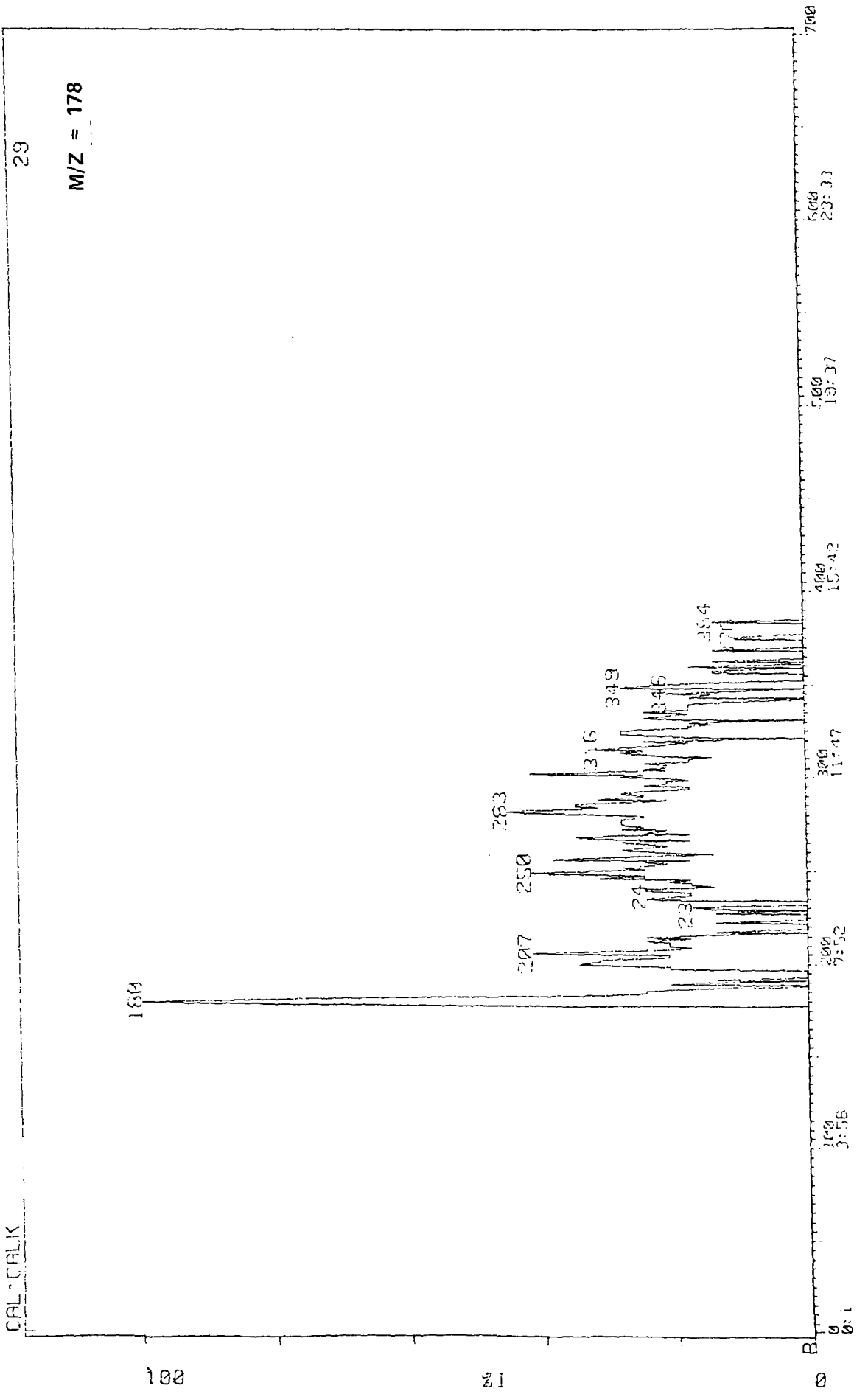
15-SEP-80

2876FC 0 -- 671 ARDMATICS 2876 FDC
A: TIC B: M=178 C: M=206 D: M=202 E: M=184 F: M=253 G: M=252
CAL: CALK



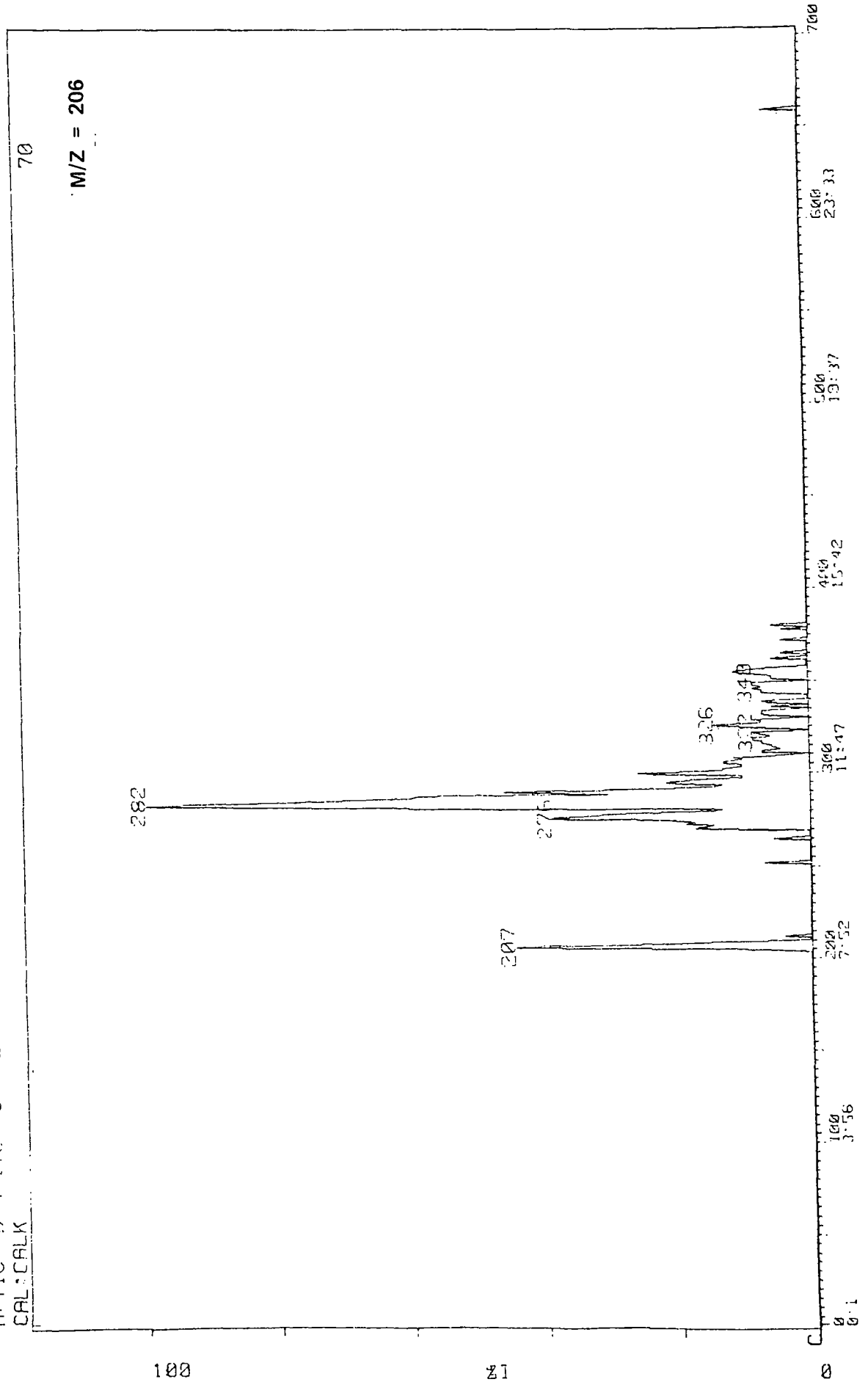
15-SEP-80

2876FC 0-671 AROMATICS 2876 FDC
A: TIC B: M=178 C: M=206 D: M=202 E: M=184 F: M=253 G: M=252
CALCALK



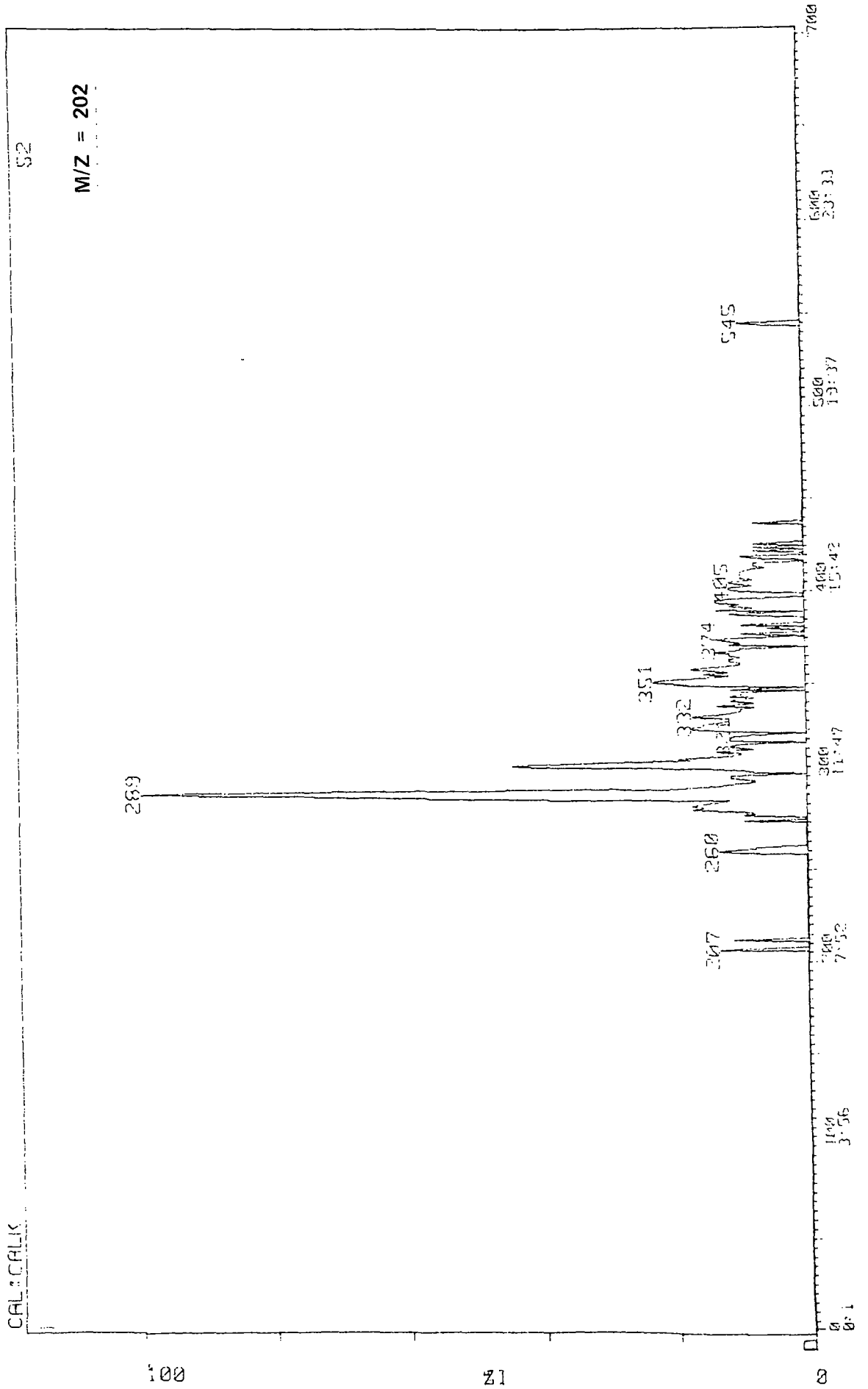
15-SEP-80

2876FC 0 - 671 AROMATICS 2876 FDC
A: TIC B: M=178 C: M=206 D: M=202 E: M=184 F: M=253 G: M=252
CAL: CALK



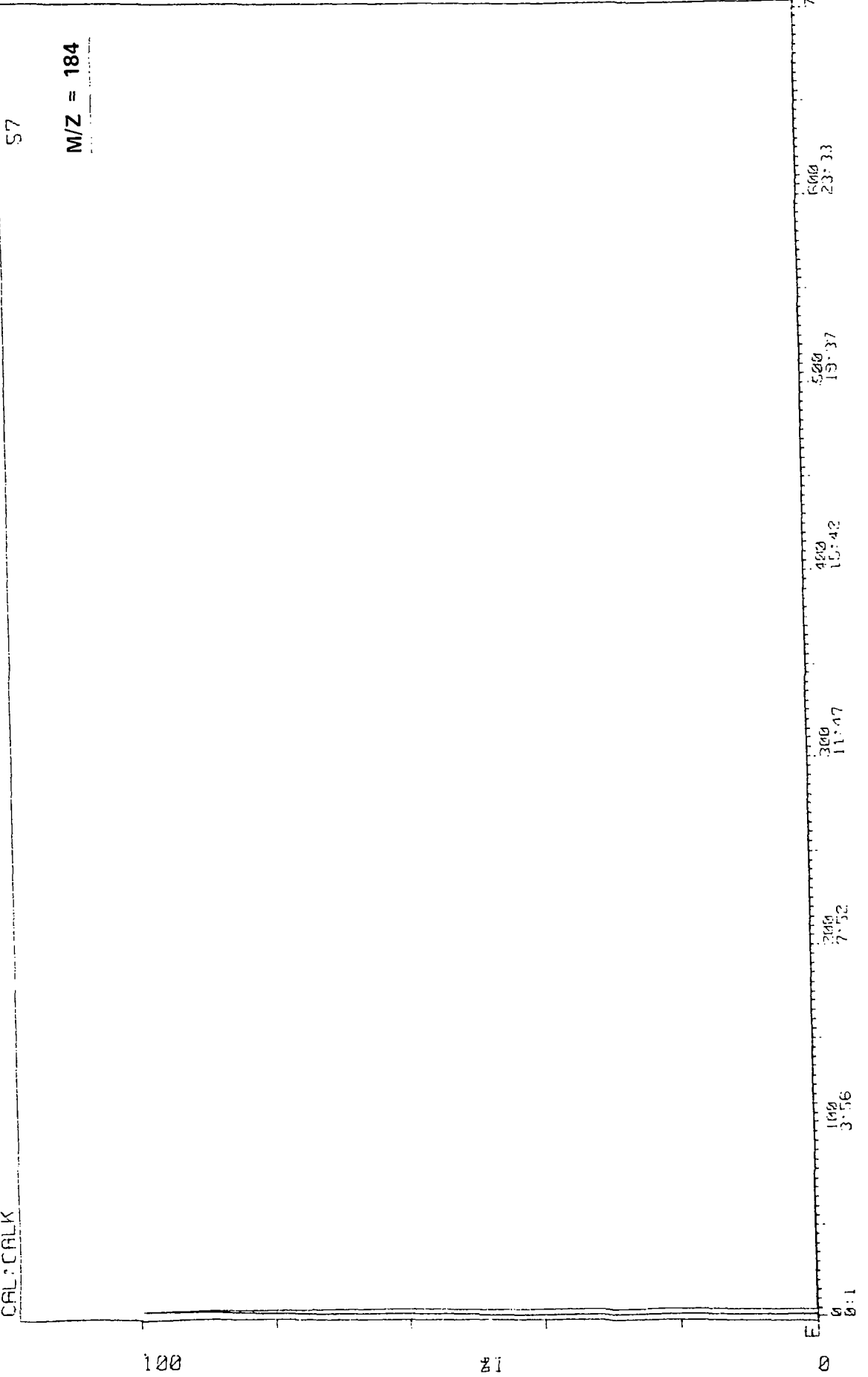
15-SEP-80

2876FC0-671 AROMATICS 2876 FID
A: TIC B: M=178 C: M=202 D: M=202 E: M=164 F: M=253 G: M=252
CAL: CALK



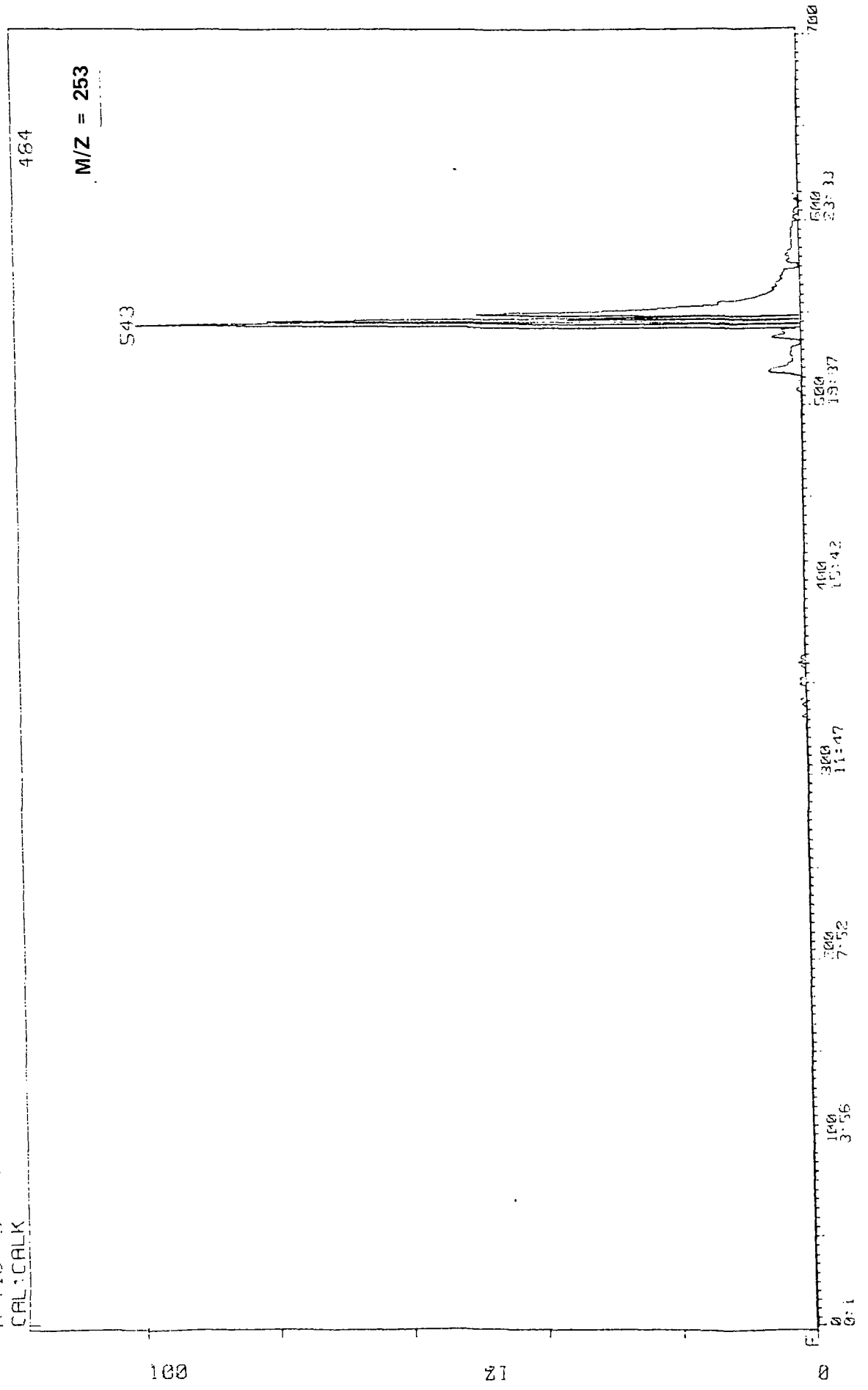
15-SEP-80

2876FC 0 - 671 AROMATICS 2876 FDC
A: TIC R: M=178 C: M=206 D: M=202 E: M=184 F: M=253 G: M=252
CAL: CALK



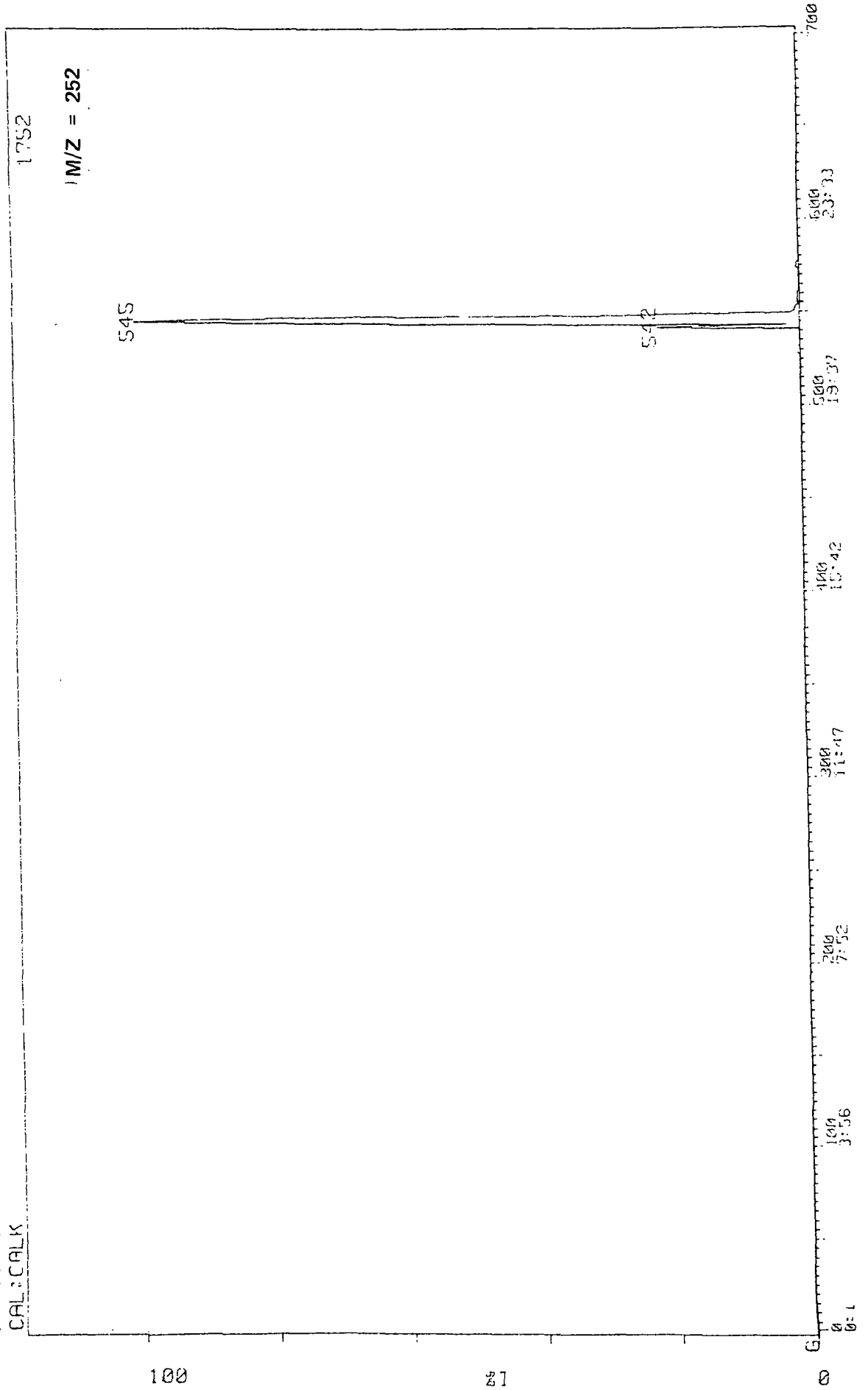
15-SEP-80

2876FC 0-671 AROMATICS 2876 FDC
A:TIC B:M=176 C:M=206 D:M=184 F:M=253 G:M=252
CAL:CALK



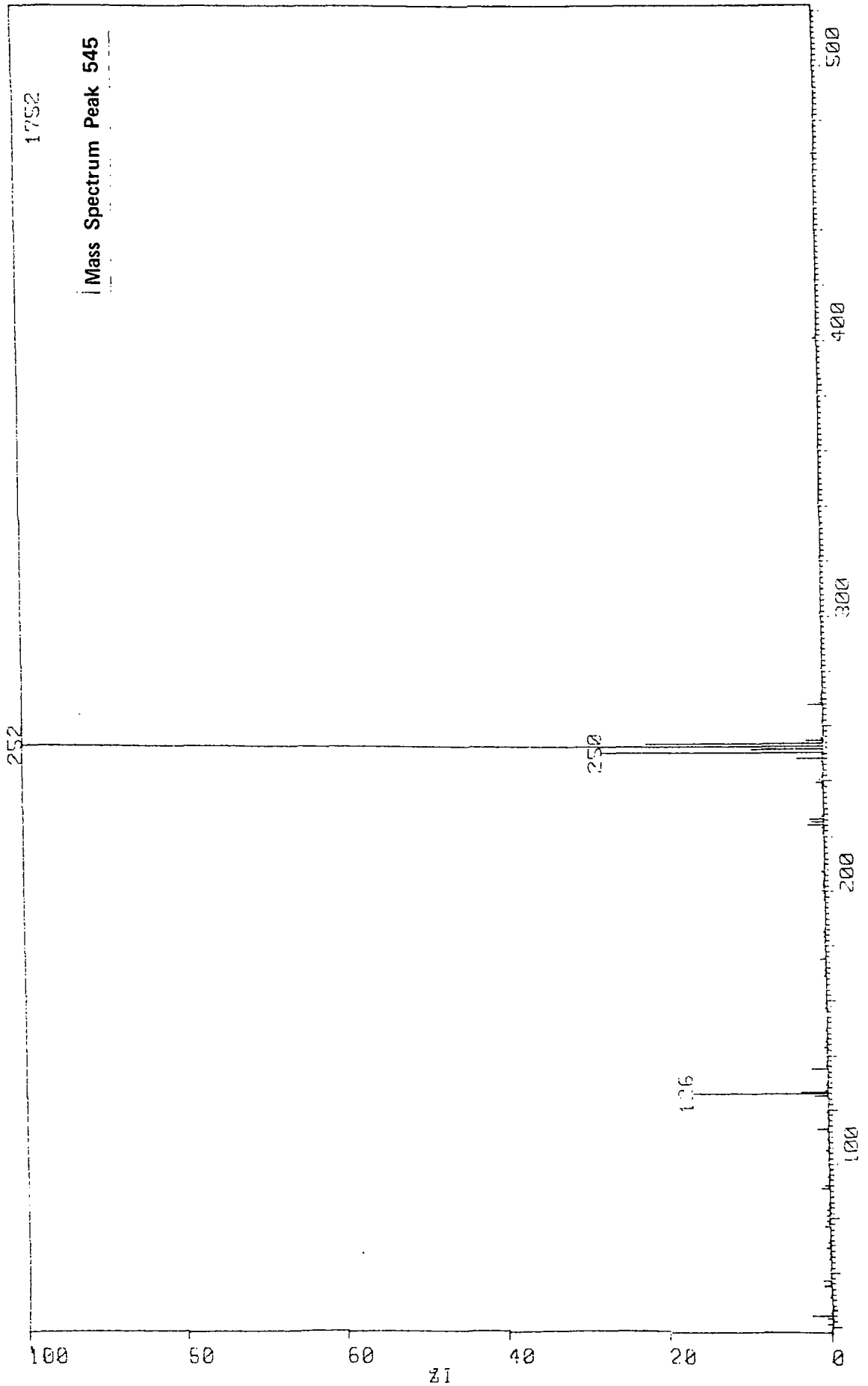
15-SEP--80

2876FC 0 - 671 AROMATICS 2876 FDC
A: TIC B: M=178 C: M=206 D: M=202 E: M=184 F: M=253 G: M=252
CAL: CALK



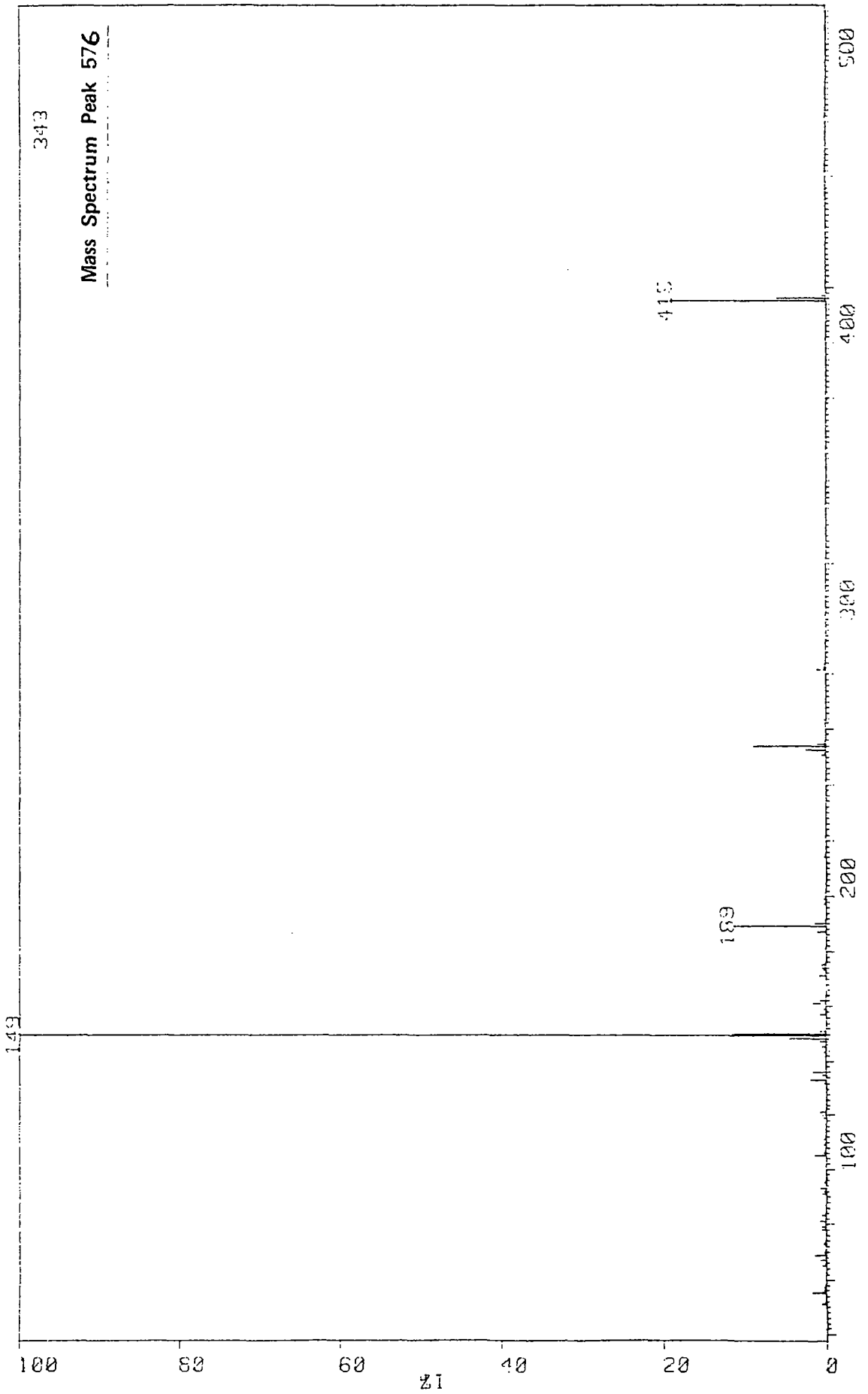
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2876FC 545 AROMATICS 2876 FDC
CAL:CALK



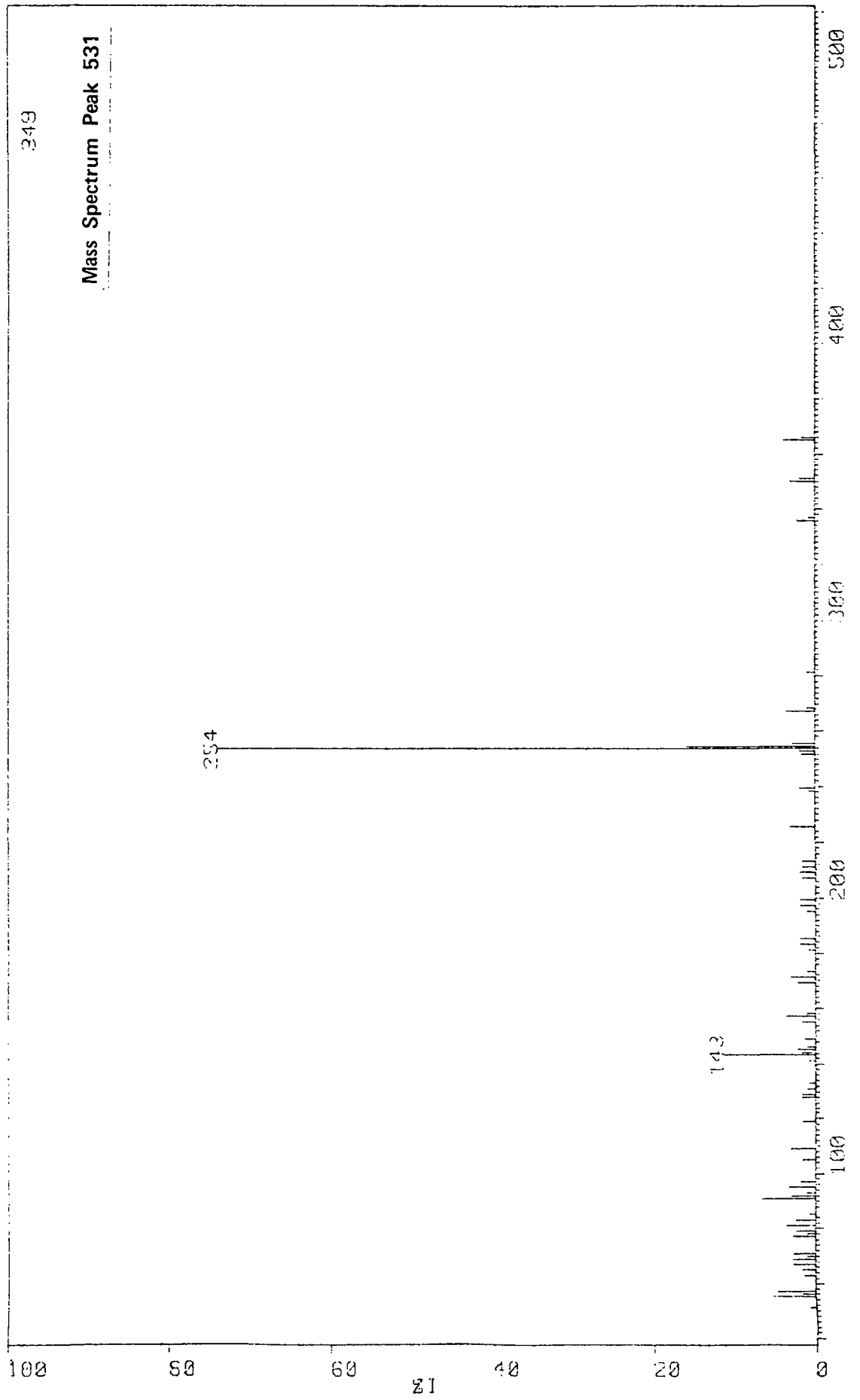
2876FC 0 572.2.6.10.10 AROMATICS 2876 FDC
CAL·CALK

15-SEP-80
22:36



2876FC 531 AROMATICS 2876 FDC
CAL:CALK

15-SEP-80



2876FC 528 AROMATICS 2876 FDC
CAL:CALK

15-SEP-80

